

Vol. 22, No. 5, September-October, 1987

May, 1988

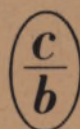
LTMRAR 22(5) 417-520 (1987)

LITHOLOGY AND MINERAL RESOURCES

ЛИТОЛОГИЯ И ПОЛЕЗНЫЕ ИСКОПАЕМЫЕ

(LITOLOGIYA I POLEZNYE ISKOPAEMYE)

TRANSLATED FROM RUSSIAN



CONSULTANTS BUREAU, NEW YORK

LITHOLOGY AND MINERAL RESOURCES

Lithology and Mineral Resources is abstracted or indexed in *Chemical Abstracts*, *Engineering Index*, and *Metal Abstracts Index*.

Lithology and Mineral Resources is a translation of *Litologiya i Poleznye Iskopaemye*, a publication of the Academy of Sciences of the USSR.

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Subscription (6 Issues)

Vol. 21: \$645 (domestic); \$715 (foreign)
Vol. 22: \$715 (domestic); \$790 (foreign)

Single Issue: \$150
Single Article: \$12.50

Mailed in the USA by Publications Expediting, Inc., 200 Meacham Avenue, Elmont, NY 11003.

POSTMASTER: Send address changes to *Lithology and Mineral Resources*, Plenum Publishing Corporation, 233 Spring Street, New York, NY 10013.

CONSULTANTS BUREAU, NEW YORK AND LONDON



233 Spring Street
New York, New York 10013

Published bimonthly, consisting of Volume 21 issues 3 through 6 and Volume 22 issues 1 and 2. Subscription price for Volume 21 is \$645, and for Volume 22 \$715. Second-class postage paid at Jamaica, New York 11431.

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A translation of *Litologiya i Poleznye Iskopaemye*

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The Russian press date (podpisano k pečati) of this issue was 9/14/1987. Publication therefore did not occur prior to this date, but must be assumed to have taken place reasonably soon thereafter.

TECTONIC ACTIVITY AND ITS LITHOLOGICAL INDICATORS
AT THE CRETACEOUS-PALEOGENE BOUNDARY

P. P. Timofeev, Yu. G. Tsekhovskii,
and V. S. Erofeev

UDC 551.24:551.3.051:551.781

In this article we show that a decrease of vertical relief forming tectonic motions was recorded over huge areas on different continents of the earth. This was reflected in the appearance of definite lithological and geomorphological indicators. This transcontinental event, whose rank is not inferior to the synchronous Laramide phase of tectonogenesis, explains many unusual geological phenomena on the described boundary.

Unusual geological occurrences at the Cretaceous and Paleogene boundary of the earth's history are noted in many publications. At that time on dry land and in the seas and oceans sediment types and rates of sediment accumulation often fluctuated, large quantities of discontinuities were apparent, and faunal and flora successions occurred. Different proposals on the cause of this have been expressed, from earthly to cosmic. Investigations in Asia and review of the literature data on other continents indicate a decrease in tectonic motions, which at that time encompassed huge areas of the earth (in this article we analyze only vertical relief forming tectonic motions, which are directly reflected in the ancient processes of sediment- and lithogenesis). This occurrence may explain the many unusual phenomena at the considered boundary.

MAASTRICHTIAN-Eocene STAGE OF THE PASSIVE TECTONIC REGIME IN ASIA

In lithologic-facies and paleogeographic investigations of late Cretaceous-Cenozoic continental deposits of Northwest Asia, V. S. Erofeev and Yu. G. Tsekhovskii [24, 25] recognized the important role of the tectonic regime in the formation of definite parageneses of sedimentary rocks, which alternate regularly with one another in vertical sections and reflect large stages in the history of the geological development of the territory in question. For one of the stages, the Maastrichtian-middle Eocene, they established a universal decrease of tectonic motion, which is reflected in the appearance of determined geomorphological indicators.

In analyzing the paleogeographic environment, the authors note that smoothing of the dry land's relief occurred at that time, and an eroded peneplain arose with a thick, practically continuous cover of weathering crust. Formation of the given smoothing surface is recorded in different tectonic structures of the dry land [24]: in the limits of the Kazakh shield, the Altai and Saur-Manrak-Tarbag orogenic zones, the Junggar Altai and the Tian Shan, and in the near-border portions of the Western Siberian and Turanian platforms. In conditions of level, slightly undulating denuded relief with a shallow erosional supply system, which did not generally cut through the mantle of weathering crust, the material generally entering the migration path was principally of fine and mature composition from the upper zone of alluvium. Therefore, the parageneses of rocks accumulated at this time in depressions of ancient dry land were exceptionally mature in their compositions: a mottled hematitic-kaolinitic association, including sequences of siliceous-kaolinitic and kaolinitic-bauxitic rocks, which gravitated to regions with a hot humid paleoclimate to the north of Kazakhstan (Fig. 1, III, IV), as well as essentially clay mottled silicon-sulfate-carbonate associations on the south of Kazakhstan in regions with an arid climate (see Fig. 1, V). The thickness of the deposits does not exceed 100-200 m.

Institute of Geology, Academy of Sciences of the USSR, Moscow. Translated from *Litologiya i Poleznye Iskopaemye*, No. 5, pp. 7-26, September-October, 1987. Original article submitted December 9, 1986.

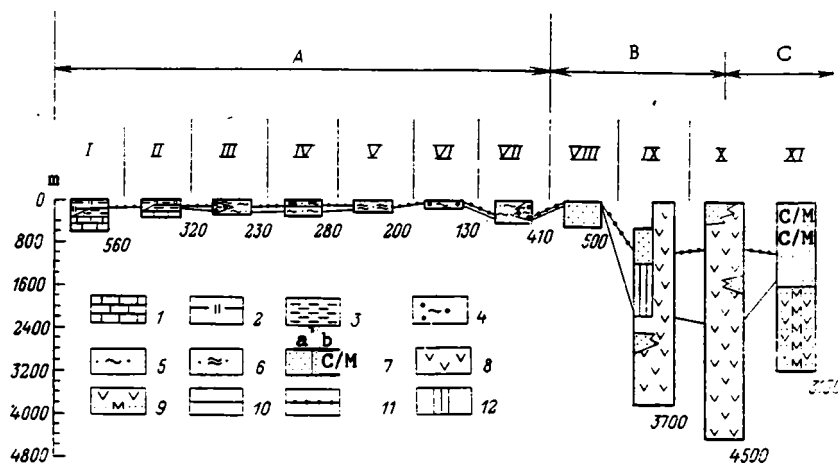


Fig. 1. Scheme of the distribution of Maastrichtian-middle Eocene rock parageneses in sections of Asia. The main parageneses: 1) lime-marl (with interlayers and lenses of silts and glauconitic-quartzic sands), marine; 2) siliceous-clay (opaka appearing clays, opokas, tripolites with interlayers and lenses of silts, glauconitic-quartzic sands), marine; 3) clay and marly clay (with lenses and interlayers of glauconitic-quartzic sands), marine; 4) kaolinitic-bauxitic, continental; 5) siliceous-kaolinitic (kaolinitic silicified and iron enriched clays with lenses and interlayers of silts and quartzic sands, continental; 6) clay smectite (with lenses and interlayers of silts and quartzic sands), continental; 7) terrigenous (a) continental sands, silts, clays, gravel, pebbles or their cemented varieties, principal immature in composition, with lenses of carbonaceous silts and clays, sometimes of brown coals; b) continental or marine sands, silts, gravelites, conglomerates, immature in composition); 8) principally volcanogenic with alternation of lavas, tuff, and tuffites, with sequences or packets of sedimentary conglomerates, sandstones, gravelites, siltstones, of greywacke composition; 9) volcanogenic-sedimentary (interbedding of marine sediments of argillites, as well as lavas, tuffs, and tuffites). The position of age boundaries in the sections: 10) between Maastrichtian-Danian and Paleocene; 11) between Paleocene and Eocene; 12) discontinuities in sediment accumulation. Region of development of rock parageneses of differing composition: A) mature (quartz-kaolinite, kaolinite-bauxite, quartz-smectite); B) alternation of mature and immature; C) immature (essentially greywacke). Regions: I) Western Siberia [12, 20, 53]; II) Turgai [19]; III) Central Kazakhstan [10, 24]; IV) Northern Prizaisan' [24, 25]; V) Southern Prizaisan' [25]; VI) Enisei ridge [5, 35]; VII) Western Pribaikal [41]; VIII) Western Priamur'e, Zeya-Bureya depression [6, 8, 11, 15]; IX) Central Priamur'e, Sredneamur' depression and its setting [8, 11, 15, 20]; X) Eastern Priamur'e, Primor'e [8, 11, 17]; IX) Sakhalin [18, 26, 42].

Several observations are in favor of a passive tectonic regime during the time of formation of the given parageneses: the principally fine and exceptionally mature composition of the component rocks, the general accumulation of the facies complex indicative of level landscapes and the absence of facies indicative of strongly separated and mountainous relief, and low rates of sediment accumulation (~ 7.2 m/million years). The Zhuravlevsk and Gan'kovsk suites, as well as the lower and middle portions of Tasarsansk and Lyulinvorsk suites [12, 19, 20, 53] formed synchronously in the adjacent Turansk and Western-Siberian seas (see Fig. 1, I, II). These are principal biogenic-chemogenic or finely detrital, mature in composition, marls, marly clays, clays, and opokas (with lenses of quartz-glauconitic sands, silts), that

are of small (up to 400 m) thickness. They also originated as a result of the entrance of material from smoothed, weakly separated erosion of ancient dry land with thick weathering crusts.

The Maastrichtian-middle Eocene stage of the passive tectonic regime continued to affect Northwest Asia in subsequent epochs, when inherited ancient weathering crusts or mature Maastrichtian-Eocene deposits were rewashed [24]. Enriching of parageneses by coarsely detrital, mature material developed strongly in the middle-late Eocene stage of tectonic motion activization, which alternated directly with the stage of passive tectonic regime under consideration. At this time a carbonaceous terrigenous association of rocks accumulated here: the Turgansk suite and its analogs [24]. Simultaneously forming in the surrounding seas were the opoka-silt-clay deposits of the Saksaul'sk, and tops of the Tasaransk and Lyulinvorsk suites, here and there with lenses of quartzic-glauconitic sands.

Data from many investigators make it possible to assume that on the Cretaceous-Paleogene boundary the weakening of tectonic activity, smoothing of relief and formation of an erosional peneplain with a thick cover of weathering crust, as well as of the correlated mature products from its rewashing, appeared in many other regions of the continent in addition to Northwest Asia. With analysis of factual data, we will also focus our attention on earlier geomorphological and lithological indicators of a passive tectonic regime. This problem was significantly eased by the fact that a large collective of geologists and geomorphologists compiled a map [31] and an explanation of it [44], where the existence was recorded of remnants of ancient smoothing surfaces and weathering crusts over large extents of the territory of the USSR. At the same time, unclarity or disagreement arose among authors on the relative ages of these surfaces and weathering crusts, their number, etc. for a number of poorly studied areas. Therefore, for further tracing of the smoothing surfaces that are interesting to us we will supplement its patterns by data on correlated deposits with the goal of controlling the conclusions of authors on those regions where similar analysis was absent or was insufficiently conducted. Unfortunately, poor study of the deposits in many regions did not always permit to us to distinguish many parageneses: bauxites comprise the exception (both as sediments and as laterites), since their places of localization are generally known from their great practical value. This is utilized for the compilation of a scheme of Maastrichtian-Eocene bauxite locations on the different continents of the earth (Fig. 2).

We will trace the apparent stage of weakening of tectonic motion on the Cretaceous-Paleogene boundary in regions of Asia with heterogeneous tectonic structure: on a platform with Paleozoic and more ancient folded basement in the west, and in regions of Mesozoic and Cenozoic foldings in the east.

We show in a scheme (Fig. 3) the contemporary distribution of remnants of the late Cretaceous-Eocene smoothing surface within the limits of Asiatic dry land of the USSR. The age of the smoothing surface that interests us, originally dated by the map authors [31] as Cretaceous-Paleogene, is given a narrower range in [44] (late Cretaceous-Eocene), which is also used in our scheme. In addition, with consideration of the data from investigators in Kazakhstan and surrounding regions [24, 25], it is divided into an essentially erosional surface (with a series of comparatively small basins, filled with Maastrichtian-middle Eocene continental deposits, which are not shown due to the Cretaceous scale) and an essentially accumulative surface (with predominance of lower Cenozoic marine deposits, accumulated in the ancient Turansk and Western Siberian seas). The age of the basal, most widely developed denudational smoothing surface of Kazakhstan and Altai is also more accurately determined. In the opinion of V. Yu. Malinovskii and S. K. Gorelov [44], here it is of Triassic-early Jurassic age, while younger (late Cretaceous-Eocene) relicts occupy comparatively small areas. The results of our investigations permit us to assert the opposite: the basal portion of the recent erosional relief in the characterized territory is comprised of residual mountains of a young, Maastrichtian-middle Eocene smoothing surface, while a Triassic-early Jurassic surface was locally preserved.

S. K. Gorelov and V. Yu. Malinovskii confirm their datings by citing the fact of covering smoothing surface and the fixing of their weathering crusts by Eocene, late Cretaceous, and early Jurassic deposits in Central Kazakhstan. And because the most ancient covering deposits appeared to be early Jurassic, the age of the weathering crusts and the correspondingly smoothing surfaces was determined as Triassic-early Jurassic. But these facts may also indicate the existence of various aged smoothing surfaces in the region: 1) pre-Eocene or early Cenozoic, 2) tending towards the base of late Cretaceous, 3) Triassic-early

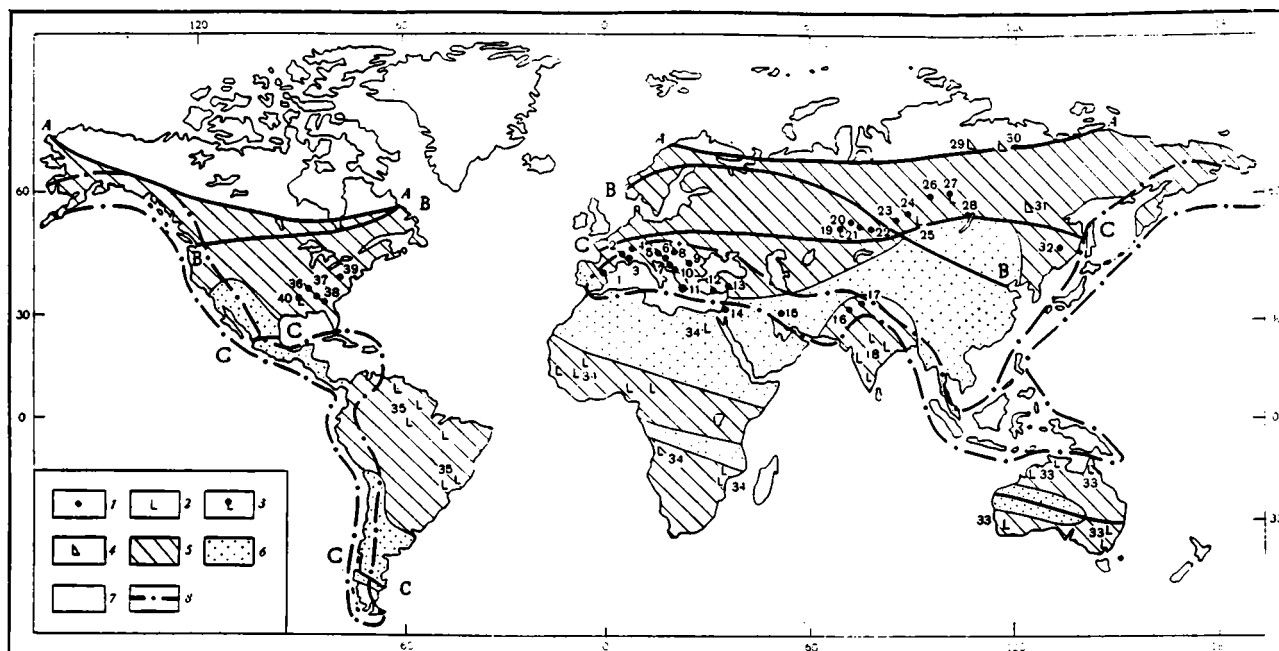


Fig. 2. Schematic map of locations of Maastrichtian-Eocene bauxites (places of localization of different bauxite occurrences or groups of occurrences are taken from data of [1, 3, 9, 30, 34, 41, 43, 45, 50]): 1) sedimentary; 2) lateritic; 3) lateritic-sedimentary; 4) appearance of lateritic bauxites (in Northern Siberia). Climatic paleozones in Eocene (after [48]: 5) hot humid (equatorial and tropical-subtropical); 6) hot arid; 7) moderately humid. Position of boundaries between humid hot and moderate paleozones: A-A) Eocene; B-B) Paleocene; C-C) Maastrichtian; 8) regions of principally Cenozoic folding with platform salients. The numbers on the map are the number of the occurrences, the appearance of bauxites or their groups: 1-11) Europe; 12-32) Asia; 33) Australia; 34) Africa; 35) South America; 36-40) North America.

Jurassic. The wide development in late Cretaceous and early Cenozoic deposits of reworking products from ancient weathering crusts (quartz-kaolinite or kaolinite-bauxite rocks) attests to the existence here of younger stages of relief smoothing and crust formation in addition to early Mesozoic [9, 29].

K. V. Nikiforova [40], considering the question on the age of the kaolinite weathering crust which crowns the smoothing surface of Central Kazakhstan, correctly notes that the base of its portion was formed here at the start of Tertiary time. It is possible that more ancient crust was been preserved here and there, but was already strongly altered by the superimposed processes of subsequent Tertiary weathering. Basically, taking into account the repeated uplifts of the indicated territories, in late Jurassic time the ancient Mesozoic weathering crust was apparently annihilated by erosion [40].

Analysis of abundant geological data confirms K. V. Nikiforova's conclusion and permits us to extend it to other regions of Kazakhstan and near-lying areas of Central Asia and Southern Siberia.

Remnants of the early Mesozoic peneplain and weathering crust could only have been preserved where they were covered by Jurassic deposits which shielded them from erosion. But a large portion of the inherited erosional regions (Altai, Kazakh shield, Northern Tien-Shan) was not covered by a mantle of Jurassic deposits, which did not enable us to distinguish large areas of development of relict early Mesozoic relief here. Since the last large inter-regional stage of extreme attenuation of tectonic motion and the smoothing of relief is dated as Maastrichtian-middle Eocene in the territory of Northwest Asia [24, 25], then that is also the age of the basal erosional smoothing surface of this region. Following other geologists, we assume that for the appearance in this region of different stages of the complete smoothing of relief and crust formation in regions of inherited erosion, only the youngest smoothing surface may be preserved (in our case Maastrichtian-middle Eocene). Relicts of more ancient surface (if they also remain here and there) merge in this case with younger,

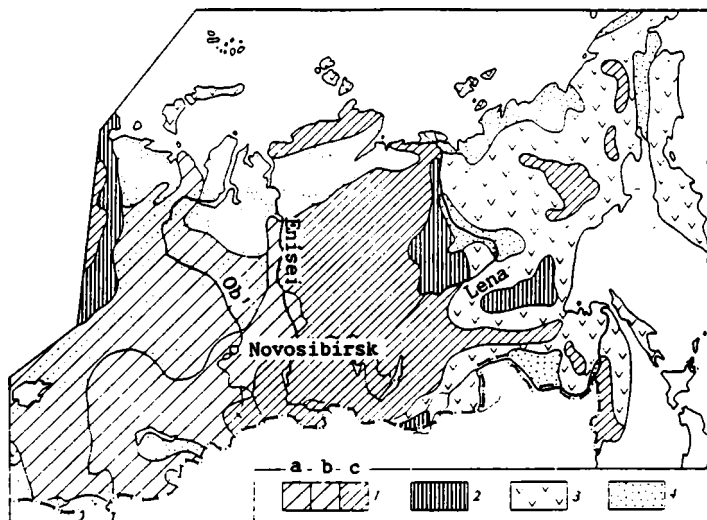


Fig. 3. Scheme of the appearance of the late Cretaceous-Eocene stage of relief smoothing and weathering crust formation in the Asiatic portion of the USSR (compiled from [31, 44], with changes and refinements). Areas of likely development of smoothing surfaces and crust formation: 1) late Cretaceous-Eocene age in Northwestern Asia [24, 25] (a) accumulative with predominance of marine deposits, b) principally erosional with continental sediment accumulation); 2) Jurassic-Cretaceous and more ancient ages; 3) Neogene age (surface of incomplete weathering); 4) area of active formation of Pleistocene accumulative plains.

forming by hypergenic processes into a single, newly formed surface. A late Cretaceous-early Cenozoic age smoothing surface on the west of the Asiatic continent is a point of view advocated by many geologists. On the extreme west (in the region of Orsk Ural and Zaural) the given smoothing surface (together with kaolinite weathering crusts) was characterized by V. V. Gudoshnikov et al. (1975). Products of its erosion are also widely developed here: lower and middle Paleogene deposits which have exceptionally mature composition.

V. I. Bgatov, V. P. Kazarinov, et al., [4] trace remnants of a late Cretaceous-Eocene smoothing surface as a clearly expressed level in the mountains of the Urals, Eastern Kazakhstan, Altai, and Sayan. For the late Cretaceous-early Cenozoic of Western Siberia and its setting, Santonian-Campanian and Eocene or Paleocene-Eocene are the most intense epochs of weathering [28, 29, 53]. Some decrease in the degree of sediment maturity in Maastrichtian-Danian indicates a strengthening of tectonic activity at this time. At the same time, V. P. Kazarinov notes that in course of that entire time span (from the end of the Cretaceous through Eocene), weathering processes proceeded with high intensity, which assisted in the accumulation of sediments of extremely similar and rather mature composition.

In Eastern Siberia, remnants of a late Cretaceous-Paleocene smoothing surface occupy a huge extent (see Fig. 3); they are often crowned by remnants of kaolinitic cover, and locally lateritic weathering crusts. In erosional-tectonic depressions, products of the rewashing of these crusts are recorded in karst depressions.

In the south of Eastern Siberia, late Cretaceous-early Cenozoic or early Cenozoic weathering crusts comprise a smoothing surface synchronous in age in the Altai, in the Pre-altai plains, and the Altai-Sayan region [25, 29, 31, 33, 44, etc.]. In the Prealtai plains, from data of O. M. Adamenko and I. G. Zal'tsman, the formation of the mature rocks of the Gan'kinsk, Sym'sk, Talint'sk, and Lyulinvorsk marine suites, with a total thickness 150-200 m is connected with their rewashing in Maastrichtian-Eocene time.

Mature continental Maastrichtian-Eocene deposits of the Karachum'sk and Taldydyurgun'sk suites up to 100 m in thickness correspond to them in the Altai mountains [24]. Occurring more to the east, the late Cretaceous early Cenozoic weathering crusts are described

by V. N. Mazilov et al., while deposits of the Sayano-Baikal uplands and the southwest portion of the Baikal rift zone are described by N. A. Logachev et al. The enrichment of the Eocene-early Pliocene Tankhoisk suite by quartz-kaolinitic minerals is connected with their rewashing.

To the north of the Altai-Sayan mountain region, remnants of late Cretaceous-early Cenozoic kaolinitic or lateritic weathering crusts are widely developed in many regions of the Siberian platform [5, 31, 34, 41, 44, 50]. The nature products of the rewashing of these crusts are often established here also.

In the limits of the Enisei ridge and adjacent regions of the Western Siberian platform, deposits of Maastrichtian-Eocene are represented [5, 35, etc.] by quartzo-kaolinitic or kaolinitic-bauxitic sequences (see Fig. 1, VI), which are distinguished in composition from the continental Antibessk and Symk suites of Danian, Paleocene-dated Murozhninsk and the upper portion of the Bol'sheketsk (Senonian) suites, with total thickness up to 300 m. In the southern portion of the Siberian platform, Cretaceous-Paleogene sedimentary bauxite-bearing sequences up to 100-200 m in thickness are known in the basins of Angara and Podkamennaya Tunguska rivers [50].

In depressions of Western Pribaikal (see Fig. 1, VII) the characteristic deposits with total thickness of 200-410 m [6, 11, 41] are distinguished in composition from the sand-clay sequence of Maastrichtian, lower Eocene-dated Kolsakhaisk suite and the lower subsuite of the middle Eocene Kamensk suite. In the latter two, bauxites are present along with wide development of quartz-kaolinitic material. The majority of bauxite occurrences (see Fig. 2) connected with erosion of weathering crusts formed here right up until middle Eocene, although their formation could have extended even longer in a reduced form.

To the west of the Siberian platform, in the basins of the Angara, Podkamennaya, Nizhnaya Tunguska, and other rivers, a great number of lateritic fragments of Cretaceous-Paleogene weathering crusts are present in Recent deposits [50] etc. These were widely developed here earlier, but subsequently destroyed by erosion.

On the north of the Siberian platform, relicts of late Cretaceous-Eocene smoothing surfaces and weathering crusts occur (see Fig. 3) right up to the shore of the Arctic Ocean (Taimyr peninsula, mouth of the Khatanga river). On the northeast of the Siberian platform, areas of distribution of the remnants of the late Cretaceous-Eocene smoothing surface are sharply reduced (see Fig. 3), but its traces are recorded here in Priabar'ya, the eastern portion of the Tunguska syncline, and the Vitimsko-Patomsk uplands [34 etc.] (publication of N. K. Kuzhel'naya, E. A. Shamshinaya, R. S. Rodin, G. N. Cherkasovaya, et al.). The findings of kaolinitic or lateritic weathering crusts (see Fig. 2), dated as Paleogene-date or Cretaceous-Paleogene, are detected in the headwaters of the Markh River, in the near-mouth portions of Linde River, in the lower flows of the Vilyui River, and in the basins of the Kotui, Maimechi, Anabar, and other rivers. Paleogene deposits, the erosion products of the given weathering crusts, have mature quartz-kaolinitic composition and are established by data of E. A. Shamshinaya et al., in the interriver region of the Markh-Tyungo rivers, on the water divide of the Bol'shaya Kuonamka and Kaly Kuonamka, in the basin of the middle flow of the Olenek River, etc. Therefore, it is possible to assume that the stage of attenuation of tectonic activity on boundary of Cretaceous and Paleogene was manifest also in the northeast of the Siberian platform, but its traces were destroyed in a majority of the cases by subsequent activation of tectonic motion.

Thus, on the west of the Asiatic portion of USSR, in the limits of the intracontinental stable region (platforms with Premesozoic folding), the stage of weakening of tectonic activity on the Cretaceous-Paleogene boundary is recorded in different tectonic structural; plates, shields and their activated parts (epiplatformal orogens). It was reflected in the development of a smoothing surface with a mantle of weathering crust within the limits of erosional relief, and in the accumulation of the products of its rewashing (small thickness, principal finely detrital terrigenous or biogenic-chemogenic deposits, of mature composition) in regions of accumulative relief.

We will consider further data on the eastern regions of Asia: the Pacific ocean active margin of the continent (regions of Mesozoic and Cenozoic folding with blocks of more ancient platforms). On the south of the east-Asian regions of the USSR, the Maastrichtian-Eocene history of development is recorded by correlated sediments of a series of depressions. On

the west of this territory, in the Verkhnezeisk and Zeya-Bureya depressions, the parts of the section which interest us are represented (see Fig. 1; VIII) by the Tsaigayansk (Maastrichtian-date), Kivdinsk (Paleocene date), and Raichikhinsk (Paleocene-Eocene) suites [6, 8, 11, 15], which have respective thicknesses of 550, 75, and 40 m. These are gray sequences of sands, silts, and clays with interlayers of pebbles, and locally coals. Semi-mature and locally mature rocks (lenses of quartzic sands and kaolinitic clays) are often developed at the base of the Kivdinsk suite.

More to the east, in depressions of Central Priamur'e and Primor'e, the structure of the upper Cretaceous-lower Cenozoic deposits is altered. In proportion to the proximity to the region of Meso-Cenozoic folding on the Cretaceous-Paleogene boundary, here tectonic motions and volcanic activity were strengthened, and thick sequences of volcanogenic-sedimentary rocks were formed (see Fig. 1, IX). For example, in Priamur'e depressions, [15] deposits of Maastrichtian-Danian (the tops of the Bol'binsk, Tatarkinsk, Malomikhailovsk, Takhobinsk, and other suites, up to 1000-1500 m in thickness) are principally represented by lavas, tuffs, tuffobreccias, etc. In the upper Paleocene-Eocene portion of the section in the Sredneamursk depression [8, 11, 15], two basic types of sections are observed. The first is composed principally of volcanogenic rocks above 200 m in thickness (the Samarginsk, Kuznetsovsk, and other suites). Sedimentary sequences dominate the composition of second sequence (the lower Bezugol'naya subsuite of the Chernorechinsk suits: terrigenous, terrigenous-carbonaceous, often coarsely detrital, 640 m thick). This is primarily an immature sediment with inclusions of different horizons of mature rocks which are enriched in quartz and kaolinite (in the middle) and upper portions of the Bezugol'naya subsuite of the Chernorechinsk suite).

Still more to the east, in Priamur'e and Primor'e [15, 17], the composition of the Maastrichtian dated deposits is principally volcanogenic, more seldom volcanogenic-sedimentary (upper portions of the Primorsk, Dorofeevsk, Monastyrsk suites, the Siayanovsk sequence etc.). Their thickness reaches 2000 m. Volcanic activity extended here in the Paleocene and Eocene [8, 11, 15, 17, etc.] and extrusive sequences were primarily accumulated (see Fig. 1, X) (the Samarginsk, Kuznetsovsk, Novopos'etsk, Bogopol'sk, and other suites) up to 1000-2000 m thick. At this time the volume of the carbonaceous-terrigenous sedimentary sequences of the lower Cenozoic is restricted in comparison with the more western regions. They form different packets in volcanogenic rocks (for example, in the Paleogene portion of the section and remain in late Cretaceous deposits, its age is determined as not the more ancient Paleogene (or Paleocene data). In Eastern Primor'e and Lower Priamur'e in Maastrichtian-Eocene, indicators of the stage of the attenuation of tectonic motion do not occur, while the character of sediment accumulation is in favor of an active tectonic regime: principally volcanogenic and volcanogenic-sedimentary sequences accumulated here at this time. These sequences are of immature composition and great (up to 4500 m) in thickness.

An active tectonic regime also prevailed on the easternmost margin of Asia, in the Cenozoic folding zone (Sakhalin island, Kamchatka peninsula, etc.). At this time, thick continental or marine sequences of sedimentary or volcanogenic-sedimentary rocks, of immature composition (often graywacke), often coarsely detrital (see Fig. 1, XI) were formed there [16, 18, 26, 35, 42, 52]. Sandstones, gravelites, siltstones, argillites, conglomerates, here and there coals, interlayers of tuffs, and tuffites alternate in their composition. On Sakhalin this is the upper portion of the Krasnoyarskovsk and Berezovsk suites, as well as the Kamensk and Nizhneduisk suites, with a total thickness up to 2000 m. They are comprised of terrigenous and volcanogenic rocks in the lower Cretaceous portion of the section, and principally of terrigenous, and terrigenous-coal bearing rocks in the Paleocene and Eocene. On Kamchatka, it is possible to distinguish the upper subsuites of the Veselovsk and Pillavayamsk Maastrichtian suite, and the Khulgunsk, Napansk, and the lower portions of the Snatol'sk suites of the Danian and Paleocene-Eocene suites, with a total thickness of nearly 3000-4000 m. Interlayers of tuffs and tuffites often occur in the late Cretaceous sedimentary sequences of these regions; in sections of the lower middle Paleogene deposits, sedimentary (terrigenous, carbonaceous) rock parageneses dominate.

In northern East Asia, the map displays a stage of tectonic stabilization basically undistinguished from the examined southern regions. It is well expressed on the west of the territory, in the region of Mesozoic folding, while on the eastern shore it fades away on approach to the regions of Cenozoic folding. Relicts of the late Cretaceous-early Cenozoic smoothing surface with remnants of weathering crusts up to 50 m in thickness are developed

(see Fig. 3) in a series of districts of the Verkhoyansk-Chukotsk mountain region [44]. The mature products of their rewashing are described here at the base of the Cenozoic [2] (for example, in the Lindensk suite). The authors note that, beginning still with the Datskian epoch, the Verkhoyansk-Chukotsk mountain country was subjected to erosional smoothing (under conditions of a decrease in tectonic activity, which was accompanied by intense chemical kaolinitic weathering. In the Okhotsk-Chukotsk mountain belt (on the boundary of the Cenozoic folding region) smoothing of relief and crust formation occurred only in discrete areas, and this was interrupted by weak extrusions of basalts.

Thus, in the early Cenozoic, stabilizations of tectonic motions and smoothing of relief enveloped a large expanse of the northeast of the USSR. But simultaneously tectonic activity of portions with separated or low mountainous relief also existed here [2], and their number increased towards the east.

Indicators of the weakening of tectonic activity on the Cretaceous-Paleogene boundary are also vividly presented in foreign regions of Asia. Smoothing surfaces of early Cenozoic age are widely developed in Mongolia [32], where they are distinguished by the name Mongolian or Khangai peneplain. V. F. Shuvalov and E. V. Devyatkin [22] established that in the territory of Mongolia, during the late Cretaceous and Paleogene, tectonic motions which were close to platformal led to the formation of a surface of erosional smoothing. In conditions of an arid or semiarid climate from Senonian to Eocene, principally finely detrital sediments of small (a few fractions of meters) thickness, and reddish or mottled color were accumulated here. The effects of volcanism were temporarily noted. Tectonic activity is already initiated here in early Oligocene.

On the basis of L. King's data [32], a stage of early Cenozoic smoothing of relief also appeared in south and Southeast Asia. For example, the Bei-Tai peneplain formed in China at this time, and peneplains with lateritic cover formed in India, comprising a large portion of the basal surfaces of the Singalezsk and Deccan plateaus. The majority of India's laterite-bauxites are often dated as Paleocene-Eocene [1, 3, etc.]; formation of the Paleocene-lower Eocene sedimentary bauxites of Kashmir and Dzhama is connected with their rewashing (see Fig. 2). Moreover (A. D. Slukin, 1983) opinions exist on the duration of lateritic bauxite formation in India in later epochs right up until recent.

In south and southwestern Asia (see Fig. 2), formation of sedimentary bauxites in Pakistan (in Paleocene), Turkey (in early Eocene), and possibly Iran and Israel (in late Cretaceous), is connected with the characterized epochs [3].

Thus, attenuation of tectonic motions is recorded on huge extents of the Asiatic continent at the end of the late Cretaceous-early Cenozoic. In the west of the territory, in an intracontinental stable region with Premesozoic folding (in the erosion zones), surfaces with thick mantles of weathering crusts formed at this time. In regions of accumulation, rock parageneses accumulated synchronously which are thin (up to 200-300 m), principally fine, mature (see Fig. 1, I-VIII), and reddish on dry land, and enriched by organogenic-chemogenic muds in the seas.

In eastern Asia, within the limits of the Pacific ocean active continental margin (the region of Meso-Cenozoic folding with ancient platformal salients), the paleogeographic environment fluctuated, which is also reflected in the character of sediment accumulation (see Fig. 1, IX-X): here are formed thick (up to 3000-5000 m) sequences of grayish, terrigenous, enriched in coarsely detrital material, generally immature sedimentary (coaly-terrigenous) or volcanogenic-sedimentary rocks. In the majority of cases they were accumulated in the presence of separated landscapes (right up to the mountains). At that time, in the west of the territory, short stages of relief smoothing were also noted, which enveloped significant areas of dry land and reflected the appearance in a series of sections of Paleocene and Eocene sequences of mature sediments, by the presence of ancient smoothing surfaces and weathering crusts. However, portions with a weakened tectonic regime and smoothed erosional relief were often alternated with separated and mountain landscapes, where active tectonic motions were apparent. It is necessary to stress that the duration of the stage of weakening of tectonic activity was shorter in the eastern portion of the Asiatic continent in comparison with its western regions. Indicators of the stage are recorded here by the mature composition of sediments only in individual portions of the Paleocene-Eocene sections and are completely unestablished in the late Cretaceous. But also in east Asia, in a short segment of early Cenozoic, smoothing surfaces smoothing and weathering crusts

occupied very large areas of dry land, and in the form of isolated portions they were traced from the southern setting of the continent to its northern margin, while in the eastern direction they sometimes reached the Pacific Ocean shore.

Traces of the stage of attenuation of tectonic motion on the Cretaceous-Paleogene boundary are completely absent only in the most eastern margin of Asia in regions of Cenozoic folding. And conversely, the Laramide phase of tectogenesis was actively apparent here at this time, accompanied by the formation of separated (locally mountainous) relief and the accumulation in continental depressions and adjacent seas of thick sequences of volcanogenic, volcanogenic-sedimentary or sedimentary mountain rocks with partial inclusions of coarsely detrital sediments of graywacke composition (see Fig. 1, XI). These active tectonic motions are recorded along the entire eastern and southeastern margin of Asia [39, 51]; they were accompanied here by large horizontal displacements of plates of continental and oceanic crust, thrust faults, manifestations of volcanism, etc.

Thus, the stage of attenuation of tectonic motion and relief smoothing on the Cretaceous-Paleogene boundary, which is apparent over huge areas of the intracontinental stable region of the Asiatic continent, universally weakens within the limits of the Pacific oceanic active margin, right up to its complete disappearance in regions of Cenozoic folding. Constriction of the time span of its appearance (Fig. 4) from Maastrichtian-middle Eocene (on the west) to discrete narrow time segments in the Paleocene or Eocene (on the east) is also recorded in this direction.

STABILIZATION OF THE TECTONIC REGIME ON OTHER CONTINENTS

The stage of weakening of tectonic activity on the Cretaceous-Paleocene boundary that is characterized in Asia is recorded by geologists on all continents of the Earth (excluding Antarctica due to its poor study).

In the following short review of data from the different continents we dwell only on the proven appearances of the same fact of the presence here of the described event and estimates of its overall scale (not touching upon the features and details of its appearance).

On the African continent, residual mountains of the early Cenozoic (African) smoothing surface occupy a significant area of recent relief, from L. King's data [32] (Fig. 5). It is best preserved in the southern and western portions of continent, generally covered by formations of kaolinitic weathering crust and often armored by lateritic alluvium which con-

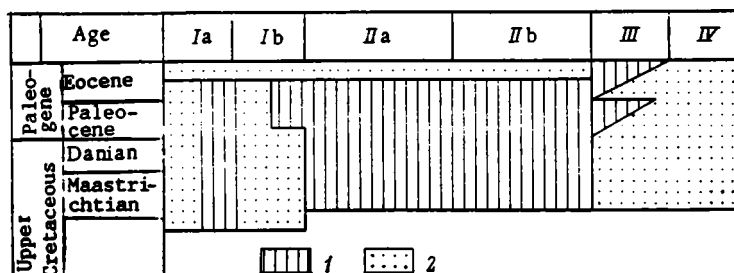


Fig. 4. Scheme of the space and time distribution of the stage of attenuation of tectonic motions on the Cretaceous-Paleogene boundary in Eurasia. 1, 2) tectonic activity (1) attenuation of tectonic motions; 2) activation of tectonic motions). Regions: I) Alpine-Himalayan fold belt, its western (Ia) and eastern (Ib) portions [21, 27, 38, 46]; II) Premesozoic with segments of Paleozoic folding of Asia (IIa) Northwest Asia [24, 25], IIb) lower portion of the Siberian platform [5, 41, 44]); III) Mesozoic folding of Primor'e and Primor'e [8, 11, 15, 17, 39, 44, 51]; IV) Cenozoic folding of Sakhalin and Kamchatka [16, 18, 39, 44, 51].

tains bauxites (see Fig. 2). S. T. Akaemov and others [1] confirm the correlation of many lateritic bauxites of Africa to the characterized smoothing surface, and cite proofs of the wide appearance of laterization processes in the late Cretaceous-Eocene (with a maximum in the Eocene). They note that beginning with the Datsk age, tectonic quiescence began, and the role of mechanical erosion decreased. The mineral composition of upper Cretaceous rocks indicates processes of chemical weathering in erosional regions beginning at this time. Fine, mature or semimature continental sediments, enriched by quartz and kaolinite, often with fragments of lateritic composition, locally silicified, were formed at this time in many depressions of African dry land. Simultaneously, the entrance of terrigenous material into adjacent seas was restricted, and chemogenic-biogenic sediments (limestones, here and there silicious, phosphatic) principally accumulated. Quartz dominates the composition of the terrigenous varieties, and fragments of laterites sometimes occur.

The paleogeographic map of the Eocene epoch from S. T. Akaemov et al. [1] comprises an excellent illustration of the assertion. It is necessary to note that in the paleogeographic environment it is possible to discern many similar traits in the character of sediment accumulation on the Cretaceous-Paleogene boundary of both Africa and northwest Asia [32]: 1) a passive tectonic regime, assisting in the smoothing of erosional expanses and the formation of mantles of lateritic-kaolinitic weathering crusts; 2) accumulation in regions of continental accumulation of fine, principally mature sediments: quartzic-kaolinitic (locally silicified) or kaolinitic-bauxitic; 3) sharp restriction of the volume of terrigenous material into intracontinental seas, and the predominance of chemogenic-biogenic (limestone, siliceous) or fine, mature terrigenous (principally clays) sediments; 4) the closeness in the age dating of the stage of attenuation of tectonic regime in the platformal portions, which began at the very end of the late Cretaceous (Maastrichtian or Danian) and was completed in the second half of the Eocene (in middle or late Eocene).

Features of the tectonic development of different regions of Africa on the Cretaceous-Paleogene boundary, assisted by the slow arching uplifts of erosional relief and formation of the African smoothing surface have been considered by a series of authors (B. M. Kryatov, S. S. Prokof'ev, Yu. P. Seliverstov, and others).

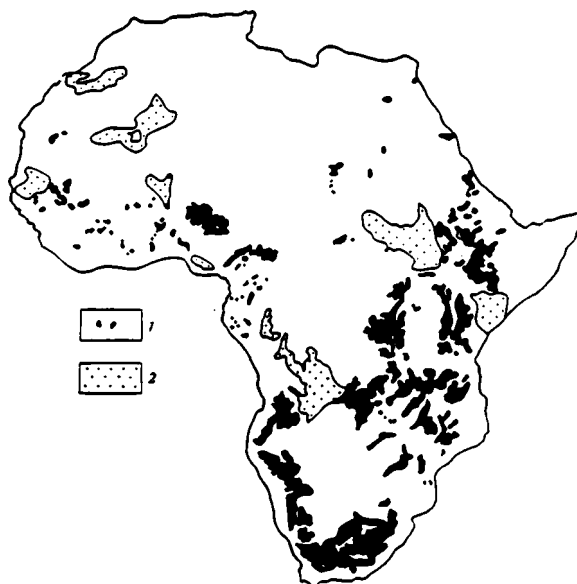


Fig. 5. Scheme of the areal distribution of the African (early Cenozoic) smoothing surface in the territory of Africa (after L. King [32]): 1) erosional smoothing surface; 2) accumulative smoothing surface.

The stage of the passive tectonic regime in the territory of Africa [1] was concluded at the end of the Eocene—start of the Oligocene, when uplift of the continent, sharp cutting of the drainage network, regression of the sea, and accumulation of sand-clay and sand sediments, principally polymictic in composition, occurred.

In Australia, the remnant mountains of the lower Cenozoic (Australian) smoothing surface are widely developed in all states [32]. It is well represented, for example, in regions of the Eastern uplands, the Western plateau, etc. [31] and often armored by ferrous, lateritic (see Fig. 2), or siliceous crusts. L. King [32] considered that the Australian surface was distributed over practically the entire continent in the early Cenozoic. The majority of occurrences of lateritic bauxites (see Fig. 2) are correlated to it, and their age is determined as Cretaceous–Paleogene–Neogene [45] or, more precisely, late Cretaceous–Eocene [1, 3, 37].

In South America, relicts of the early Cenozoic (Sulameriisk) denudational smoothing surface, in L. King's opinion [32], occur on the extensive eastern (platform) portion of the continent, from the Amazon river to Patagonia, inclusively. This surface is more weakly expressed on the north of the continent, but it is recorded in Colombia and Venezuela. The Sulameriisk surface of South America comprised a base for the formation of recent relief. Connected to the crowning weathering crust are the majority of alluvial bauxite occurrences (see Fig. 2) of Surinam, Guyana, Guinea, which have a late Cretaceous–Eocene data [1, 3] utilized for formulation of the scheme. However, opinions also exist on the predominance of a late Pliocene age for these bauxites.

In North America, the remnant mountains of the early Cenozoic (Shuliisk) smoothing surface [32] are widely developed in the territories of the Appalachians, Great Plains, etc. This surface is distributed almost universally in the northeast portion of the continent and the adjacent islands (right up to South Greenland). Rewashing of the lateritic weathering crusts is connected [3, 47] with multiple occurrences of Paleocene–lower Eocene sedimentary bauxites in the western regions of the USA (see Fig. 2).

In North and South America, indicators of the stage of weakening of tectonic activity are recorded in the stable ancient platforms of the central and eastern portions of the continents. In the active margins of their western portions (regions of Meso–Cenozoic folding and adjacent activated sections of more ancient platform) the given indicators fade away. The Laramide phase of tectogenesis was apparent here on the Cretaceous–Paleogene boundary, accompanied by orogenesis, volcanism, and folding, and immature terrigenous or volcanogenic sequences of great thickness (often up to several thousand meters) accumulated, with wide development of coarsely detrital rocks. This has been noted by many geologists (A. Irdli, P. N. Kropotkin, and K. A. Shakhvarstov, etc.).

On islands of the Caribbean basin in the Maastrichtian–Eocene epoch, the formation of thick weathering crust and the products of its rewashing is recorded in Cuba [7].

In Europe, the characterized stage of attenuation of tectonic activity is widely recorded both in the eastern and western regions [31, 32, 44, etc.]. Materials on Western Europe present the greatest interest, where it was apparent in the north (platform with Paleozoic folding) and south (in the Alpine fold belt). Remnant mountains of the early Cenozoic smoothing surface are widely developed in the territories of Spain, France, Britain, Germany, and Scandinavia. The formation of multiple occurrences of sedimentary bauxites in Spain (Paleocene), France (Senonian–Danian), Rumania (Senonian), Hungary (Senonian, Paleocene, and middle Eocene), Bulgaria (Senonian, lower and middle Eocene), Albania (lower and middle Eocene), and Greece (middle Eocene), is connected with the erosion of the lateritic weathering crusts which armor this surface [3] (see Fig. 2).

Stabilization of late Cretaceous–middle Eocene tectonic activity was expressed in the character of the sediment accumulation in the Mediterranean Sea [27]. Along the northern setting of the African platform and the adjacent Alpine folding zone, peaceful marine environment of sediment accumulation predominated in a majority of the region, and principally chemogenic–biogenic (limestone–marl), here and there terrigenous (primarily clay) sediments formed, up to 600–1000 m thick. At the end of the Eocene, the stage of activation of tectonic motions was recorded here. This was reflected in the appearance of nonconformity between sedimentary complexes, and led to an increased role of the terrigenous components in the composition of the deposits, regression of the sea, and accumulation of thick, coarsely detrital sequences.

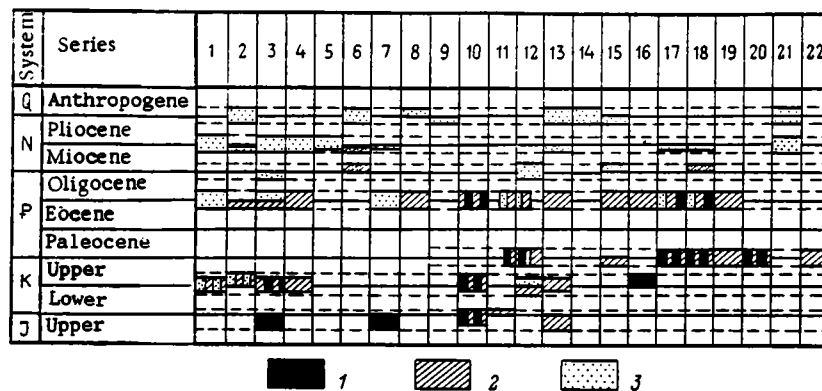


Fig. 6. Scheme of the space and time distribution of olistostromes in the Alpine fold region after the data of M. G. Leonov [46]: 1) ophiolitic and ophiolitic-clastic olistostromes; 2) olistostromes connected with flysch; 3) olistostromes connected with molasse. Numbers on the scheme refer to regions: 1) Pyrenees; 2) Betic Cordilleras; 3) Northern Apennines; 4) Southern Apennines; 5) Sicily; 6) North Africa; 7) French Alps; 8) Swiss Alps; 9) Austrian Alps; 10) Dinaric Alps; 11) Outer Carpathians; 12) Inner Carpathians; 13) Balkans; 14) Crimea; 15) Greater Caucasus; 16) Lesser Caucasus; 17) Western Turkey; 18) Eastern Turkey; 19) Iran; 20) Oman; 21) Pamirs; 22) Himalayas.

Examining features of bauxite accumulation in the Alpine orogenic region of the Mediterranean, D. Bardoshshi [3] confirms that their massive formation occurred in a stage of weak tectonic activity, their formation gravitated to relatively stable portions, and it was accompanied by the accumulation of organogenic-chemogenic limey sediments in the seas.

The paleotectonic investigations of M. G. Leonov [46] indicate the attenuation of tectonic motions on the Cretaceous-Paleogene boundary within the limits of the entire Alpine-Himalayan fold belt. From the cited scheme of olistostrome distribution (indicators of an active tectonic regime), it is apparent that their minimal development occurs in the time span from the end of the late Cretaceous to the middle Eocene, (Fig. 6). These formations do not occur in middle and upper Paleocene and lower middle Eocene deposits, while in late Cretaceous-lower Paleocene, they are absent in the western regions (from the Pyrenees to the Austrian Alps) and are apparent in the central and eastern regions (Dinaric Alps, Carpathians, Turkey, Iran, Oman, and the Himalayas).

During the considered epoch, in the Alpine-Himalayan fold belt, portions where attenuation of tectonic activity was recorded (relatively stable zones) alternated with zones of active downwarping. The Carpathians serve as an example of the latter, where during the Mastrichtian-middle Eocene sequences of terrigenous flysch accumulated to several thousands of meters in thickness. They are locally intermixed with gravellite-conglomerates [21]. Thick sequences of terrigenous or carbonate flysch were formed at this time in a series of regions of Alps, Apennines, Pyrenees, etc. [38].

In the territory of Europe, in distinction from Asia, the characterized stage of weakening of tectonic activity on the Cretaceous-Paleogene boundary was reflected not only in the stable platformal regions of the continents, but also on their active margins, in the limits of many regions of Alpine-Himalayan fold belt. Similar to the Asiatic continent, restriction of its duration is established here. It is determined in the western regions of the belt as upper late Cretaceous-middle Eocene, while in the east as middle Paleocene-middle Eocene.

Thus, attenuation of tectonic motions and smoothing of relief in late Cretaceous-early Cenozoic was manifest over huge expanses of the earth, and it bore a transcontinental character. The question of the duration of the considered stage, the precise time of its appearance in the different regions and continents of the earth, was decided by geologists with the application of various systematic procedures, and therefore their opinions do not always agree. The dates of continental sequences are often given over a wide range due to their

weak saturation by paleontological remnants, for example, Cretaceous-Paleogene, late Cretaceous-Paleogene, or early Cenozoic, etc.). In such regions where the stratigraphy of continental sequences is well worked out, different authors often give extremely close ages. As was noted earlier, the position in time of the upper age boundary of the characterized stage varies little and is generally determined as the end of Eocene or middle Eocene (Northwest Asia, Northeast Asia, Mongolia, Africa, etc.).

Conversely, dating of the lower boundary of the stage is rather undefined. In the Alpine-Himalayan fold belt its position within the limits of the tops of the late Cretaceous is not exactly known, but in the majority of cases in Eurasia it is dated as no older than Maastrichtian, possibly approaching upper Campanian (in regions of Northwest Asia and the south of the Siberian platform). In isolated cases it is descends (in Mongolia) [22] to the Senonian. However, we do not exclude the possibility that the Mongolian Maastrichtian-Eocene stage of attenuation of tectonic motions is combined with the similar, more ancient stages recorded by many authors in the western regions of Asia, where they are distinguished from one another by the comparatively short time intervals of somewhat revived tectonic activity. Beyond the limits of Eurasia, an accurate position of the lower boundary of the described event is generally unrecorded within the limits of the late Cretaceous. It is true for Africa [1], the onset of tectonic repose is noted from Datskian time. In Australia, the stage when formation of the ancient peneplain was completed is limited to the most initial Cenozoic (occurrences of laterite-bauxites of Kimberly, Dzhoklinik, and others [45]). In North America, this boundary is located at very end of the late Cretaceous or the start of the Cenozoic, which is confirmed by the accumulation of sedimentary bauxites, beginning with the Paleocene [3]. In Cuba, the epoch of thick chemical weathering is dated as Maastrichtian and Eocene [7].

In the resulting scheme (see Fig. 4), the show the space and time positions of the stage of attenuation of tectonic motion in different structural regions of Eurasia.

On the whole it is shown that for the different continents the most reliable age for the stage of decrease of tectonic activity is Maastrichtian-middle Eocene, with a possible onset in upper Campanian or slipping of the lower boundary into the second half of the Paleocene-start of the Eocene, and a corresponding restriction of its temporal interval. In the opinion of Yu. G. Leonov and V. E. Khaina [46], slippage in the datings of global events in different regions of the earth within the limits of the determined age interval may be considered a natural phenomenon.

Regardless that for the majority of the continents the complete characteristics of the given event and the appearance of the exact areas of the phenomena are a problem for further investigations, several general regularities have already been outlined in the initial stages of their study. It is established that the attenuation of tectonic activity is most vividly observed in stable portions of continents: platforms with Premesozoic folding. For example, in Northwest Asia it is expressed both in tectonically peaceful sections (platforms, shields) and also in activated sections (epiplatformal, orogenic).

The event is rather clearly recorded also in several tectonically active regions (for example in a series of regions of the Alpine fold belt), where it is possible to see its indicators, as well as in the stable portions of continent. At that time, segments were often preserved from active tectonic activity here, where the Laramide phase of tectogenesis was apparent.

ATTENUATION OF TECTONIC MOTION IN MARINE AND OCEAN REGIONS

In considering the Maastrichtian-middle Eocene stage of tectonic stabilization on the different continents of the earth, we were almost unconcerned with the extensive regions of marine and oceanic sediment accumulation (exclusive of the portions of intracontinental seas adjacent to dry land). It is necessary to give special attention to the solution of these problems in later work. However, data are already available at the present time which indicate the possibility of fixing the characteristic event in marine and oceanic regions. For example, it was noted earlier that small thickness, principally chemogenic-organogenic (carbonate, siliceous) sediments or fine, essentially clay muds, sometimes composed of lenses of mature quartzo-glaucinitic sands were accumulated in the Maastrichtian-middle Eocene seas washing the peneplainized dry land in Northwest Asia and Africa. In this relation are very important conclusions of geologists who are directly studying marine and oceanic deposits.

For the late Cretaceous-Paleocene stage of oceanic sediment accumulation, A. P. Lisitsyn et al. [36] note the features of sediment compositions and the differences in the character of ancient processes of sedimentation and lithogenesis in comparison with middle late Cenozoic time. Oceanic terrigenous sedimentation weakened sharply at this time, and biogenic (principally carbonate) developed widely. As the authors of the above cited article confirms, this was a genuine "kingdom of carbonate deposition," and carbonate rocks often contained almost no terrigenous contaminants (the of CaCO_3 content often reached 98%). Minimal rates of sediment accumulation and minimal values of the absolute masses of accumulating terrigenous and carbonate material are a characteristic of the given time. In addition, the maximum distribution of discontinuities in the sediment accumulation over the entire history of ocean development falls in the Paleocene (nearly 80-90% of deep water drilling cores contain Paleocene discontinuities of sediment accumulation).

The conclusions of A. P. Lisitsyn et al. are very similar to the results to the results of the investigations of A. B. Ronov, V. E. Khain, and A. N. Balukhovskii [49]. In their data, the Cretaceous-Paleogene boundary was reflected in a sharp reduction in the rates of denudation of dry land, as well as in the overall volumes of accumulating deposits and rates of sediment accumulation on dry land, in the seas, and the oceans. A minimal value of these quantities over the course of all Meso-Cenozoic history falls in the Paleocene. Wide development of carbonate formations and restriction of terrigenous formations is noted at that time is noted. A. P. Lisitsyn et al., [36] cite the following causes as an explanation of these features of sediment formation in the late Cretaceous-Paleocene epochs: restriction of the area of water collection (continental dry land), due to intensive transgression of the sea (in the late Cretaceous nearly 55% of present day dry land was covered by the sea); warmer climate; absence of glaciation; geographic features of the position of ancient dry land (the location of a large portion of it in zones with temperate and arid climates and a comparatively small portion in the equatorial zone); blocking of the oceans by a system of island arc seas.

In our view, still another no less important, and possibly also determining cause existed at the same time: the attenuation of tectonic motions: the smoothing and reduction of huge expanses of dry land in limits of all of its continents. This level dry land, slightly elevated above sea level and covered by a mantle of weathering crust, promoted the input of an extremely small mass of material into the surrounding seas and oceans, while the role of the products of chemical destruction of mountains grew sharply in its composition and the role of products of physical weathering was reduced. This is in good agreement with the reduction in the oceans of areas of terrigenous material accumulation, and the sedimentation of principally chemogenic-biogenic, essentially carbonate, locally siliceous muds. From a similar position one may easily explain the low total rates of sediment accumulation in the ocean basins, the presence of multiple discontinuities of sediment accumulation, and the deficit of terrigenous material in the composition of oceanic carbonates.

This is in agreement with the data of P. P. Timofeev and V. V. Ereemeev on the regularity of ancient sediment accumulation in regions of the Atlantic ocean [47]. Upper Cretaceous-Paleogene deposits were characterized in wells in the Western and North Atlantic (legs 41 and 48 of the Glomar Challenger) which were drilled in various structures (uplifts of Sierra Leone, at islands of the Gold Coast, the continental slope of Western Sahara, the Morocco deepwater basin, the Bay of Biscay). For Campanian-middle Eocene sediment accumulation, reduction of terrigenous material input is noted in a well sited on the continental slope of Northwest Africa. It is seen from the sections cited in [47] that in majority of Campanian-middle Eocene deposits wells are distinguished from underlying (Aptian-Santonian) and overlying (late Eocene-Oligocene) rocks by a higher content of organic-chemogenic components (carbonate, siliceous) and a reduction of terrigenous components (sand, silt, clay) or by a finer composition in others. These above regularities were not observed in only one of the wells: here carbonate-siliceous rocks comprised its entire section, from Jurassic to Pleistocene inclusive-ly.

The unusual history of the geological development of the northwest portion of the Atlantic ocean on the Cretaceous-Paleogene boundary was expressed after the data of I. O. Murdmaa et al. [13], in the appearance of determined sedimentary formations, traced from mid-Atlantic ridge to the continental margin of North America. Among them, along with the carbonate formations of the continental margins and the mid-Atlantic ridge is widely represented a mottled clay formation, developed within the limits of the ancient ocean floor and in the eastern

portion of the continental margin. It is most typically of the Campanian-Maastrichtian suite, although it often has a more ancient age. In a series of regions (the Somme plain; the mountains of New England) this formation is also noted in early Cenozoic (Paleocene) deposits. In other regions, in a portion of the Paleocene and the lower half of the Eocene, discontinuities in sediment accumulation occur, or the accumulation of carbonate and siliceous-carbonate sequences is recorded.

The mottled clay formation is tinted in reddish-mottled tones, has a clay (montmorillonitic, often with mixture of kaolinite) composition, and amid detrital rock varieties it often displays quartzic silts and sands (on the continental slope). The rocks are often distinguished by an increased content of iron and aluminum oxide and by a small content of organic material. The authors note that factors necessary to produce this formation includes: extremely low rates of sediment accumulation and biologically productivity in the muds, the presence of multiple sediment accumulation discontinuities and of the horizons of underwater mud transformations connected with them, which promote the appearance of red color in the rocks, and the genesis of iron and iron-manganese crusts. Enrichment of muds by kaolinite within the limits of the continental margin and the appearance of quartzic sands are connected with the wide development in kaolinite-lateritic weathering crusts adjacent peneplainized dry land.

Consequently, on the Cretaceous-Paleogene boundary, in parallel with the wide accumulation of the continental red-mottled clay rock parageneses on dry land (humid or arid), the red-mottled formations also arose in a series of portions of the ocean. The continental and oceanic mottled formations are principally of thin clay composition, with red tints, increased iron oxide contents, low value of organic material, and enrichment of the terrigenous components by quartz and kaolinite. Extremely low rates of sediment accumulation and multiple discontinuities are noted during the formation of the oceanic and continental mottled sequences. The sediment discontinuities were often recorded in continental sequences by horizons of red-mottled mineral soils, while in oceanic deposits they are found in red horizons of similar sediment formations. Smoothed dry land covered by areal weathering crusts played an important role in the formation of the mineral compositions, serving as a supply of mature terrigenous material.

For the genesis of similar environments of oceanic sediment accumulation, it is true that it is necessary to suppose attenuation of activity of tectonic motions also within the oceanic regions: smoothing of subaqueous erosional relief, reduction of the volume of edaphogenic material, mobilization in areas of underwater erosion, etc.

The cited example show that the direction of investigations is already entirely justified, with its aim of discovering the indicators of the stage of attenuation of tectonic motions in marine and oceanic regions of the earth.

RANK OF THE MAASTRICHTIAN-EOCENE STAGE OF THE PASSIVE TECTONIC REGIME

In summing up the characteristic Maastrichtian-middle Eocene stage, it is necessary to stress the distinct fixation of two tectonic events at this times: 1) the weakening of tectonic activity in some areas, and 2) the active manifestation of the Laramide phase of tectogenesis in others completely studied by geologists. We will attempt to estimate the approximate ranks and scales of the appearance of each of these events in different tectonic regions of the continents.

Attenuation of tectonic motions on the Cretaceous-Paleogene boundary, judging by lithological indicators, is probably reflected over a large part of the area of continental blocks. It is more clearly recorded in tectonically stable regions with Premesozoic folding, but this event was also often apparent in tectonically active regions to a greater or lesser degree (for example, in Mesozoic units of eastern regions of the USSR, some regions of the Alpine-Himalayan fold belt, etc).

In comparison with the previous event, the Laramide phase of tectogenesis touched upon significantly smaller areas of continents. It was universally attracted only to tectonically active regions of Cenozoic folding (and platformal portion immediately adjacent to them) and was particularly vividly apparent within the limits of the Pacific Ocean fold belt. But the given event was reflected far from universally in these tectonically active regions, or it was reflected in a strongly weakened form (for example in the Alpine-Himalayan fold belt).

Evaluating the two synchronous events which appear on the continents at the Cretaceous-Paleogene boundary, it is possible to see that areas of stabilization of tectonic activity were not inferior to regions with active tectonic regime, and conversely, they probably significantly outnumbered them. A hypothesis arises on the possibility of the assignment of the Maastrichtian-middle Eocene stage of attenuation of tectonic motion to the category of a global event. The presence of extensive regions with manifestation of the Laramide tectogenetic phase noted above at first glance attest against this hypothesis. However, in recent years the interpretation of the concept of a global event has also undergone changes. For example, as Yu. G. Leonov and V. E. Khain wrote: "It is more interesting and promising to consider an orogenic event (phase, epoch) to be global not when it is established by geological data over all the parts of the Earth without exception (which most likely does not happen), but instead when the totality of its appearances (large area, distribution in different regions separated from one another) may be explained only as the result of a simultaneous general process influencing the entire Earth, although clear and identical traces do not necessarily remain everywhere" [46, p. 13]. From this point of view, the attenuation of tectonic motions on the Cretaceous-Paleogene boundary, as represented by us, may be completely assigned to the global category.

L. King most clearly formulated conclusions on the early Cenozoic and more ancient global stages in the weakening of tectonic motions and smoothing of relief in the earth's history [32]. In the USSR, representations of similar epochs that are globally apparent or that in any case touch upon large portions of dry land were expressed by V. P. Kazarinov [28, 29], V. P. Petrov [43], I. P. Gerasimov [23], A. V. Sidorenko [44], and others. These earliest presentations, often still too hypothetical and idealized, were subjected to valid criticism. In particular, it has been learned that similar events are far from universally apparent, their boundaries are often slipping, the character of their appearance often varies in different tectonic structures, etc. In addition, the representations of L. King, I. P. Gerasimov, et al., were based mainly on geomorphological methods of investigation, without the proper inclusion of data on correlated sediments. Therefore, reliability of the dating and comparison of smoothing surfaces in different parts of the earth, as equal facts of the presence of stages of a global weakening in tectonic activity remains debatable.

The conducted wholly guided investigations of one of the similar stages in the attenuation of tectonic activity (on the Cretaceous-Paleogene boundary) confirm its global character (the meaning of the globality of an event is from Yu. G. Leonov and V. E. Khain [46]). Events of a similar sort, in L. King's opinion [32], reflect general subcrustal processes on planet as a whole.

It is probable that questions on estimates of the scales of the manifestations and clarification of the rank of the more ancient stages of the stabilization of tectonic activity, the smoothing of relief and the formation of areas of weathering crusts also merit further investigations. Regional, intraregional, transcontinental, and even global events may probably be included in their number. For the appearance of the latter in the Mesozoic, it is necessary to give first and foremost attention to the to the early middle Triassic, middle late Jurassic, and early Senonian stages of the earth's development.

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DIASPORE BAUXITES OF WESTERN CUBA

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UDC 553.492.1(729.1)

The chemical composition and mode of occurrence of diaspora bauxites of Western Cuba are described. Some problems of their genesis are considered.

In 1976 boulders and blocks of hard bauxites were discovered in the west of Cuba in the province of Pinar del Rio near the base of the Pan de Guajaibón and Sierra Azul hills composed of Cretaceous carbonate rocks [9]. Subsequent explorations made it possible to qualify the western part of the bauxite area as a deposit of high-grade diaspora bauxites, a description of which is given below. Later, pebbles and boulders of similar bauxites were found along river valleys and in depressions of the central part of the Pinar del Rio Province. Most of the newly discovered occurrences have no spatial relation to the Pan de Guajaibón-Sierra Azul bauxite zone (Fig. 1).

Geological Conditions of Bauxite Localization. The Pan de Guajaibón deposit is confined to the mogote (hill) of the same name, which topographically, is a conspicuous elevation with relative heights of 250-600 m. A characteristic feature of the tectonic structure of the region is the combination of intricately interwoven autochthonous and allochthonous structures and the presence of numerous disjunctive displacements of the thrust fault, normal fault, strike-slip fault type. The oldest geological formations are basalts and basic lavas of the Encrucijada suite of Early Cretaceous age (Figs. 2 and 3). The mogote proper is composed predominantly of carbonate deposits of the Guajaibón suite, whose age was determined by fossil assemblages as Albian-Cenomanian [6]. The suite is divided into three subsuites: 1)

*Deceased.

Arkhangel'sk Geological Production Association. Translated from *Litologiya i Poleznye Iskopaemye*, No. 5, pp. 27-35, September-October, 1987. Original article submitted November 11, 1985.

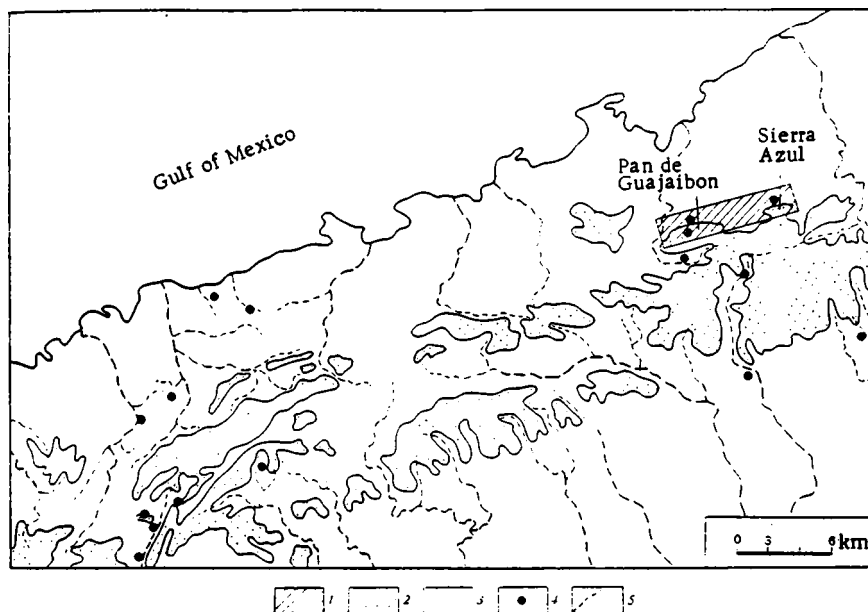


Fig. 1. Schematic representation of the distribution of diaspore bauxites of Western Cuba. 1) Pan de Guajaibón-Sierra Azul bauxite area; 2) mountainous relief; 3) lowland relief; 4) bauxite occurrences; 5) rivers.

a lower carbonate subsuite consisting of light-gray limestones and dolomites; 2) a middle terrigenous red-colored subsuite with hard, dense bauxites; and 3) an upper carbonate subsuite represented by dark-gray argillaceous limestones. The total thickness of the suite reaches 600 m, and the thickness of the bauxite horizon is 25-30 m. A detailed lithologic-facies study of deposits of the Guajaibón suite has shown that the carbonate rocks were formed in marine lagoons under conditions of repeated outcropping [7].

At the base of the mogote are developed deposits of Late Cretaceous, Paleogene, and Quaternary age. Late Cretaceous formations are represented by three suites: 1) the Quiñones suite - polymictic and calcareous sandstones, siltstones, argillites, beds of limestones, gritstones, and conglomerates, lenses of basic lavas; 2) the Via Blanca suite - polymictic and calcareous sandstones, siltstones, gritstones, and conglomerates; 3) the Cacarajicara suite - calcareous sandstones, gritstones, and conglomerates.

The relationships between suites have not been clearly established; their age within the stages is rather arbitrary.

Paleocene deposits are composed of the Manacas olistostrome - polymictic and calcareous sandstones, siltstones, limestone beds, basaltic andesite lenses, fragments, blocks and olistoliths of carbonate and terrigenous rocks.

Quaternary formations are represented by clays, loams, and loamy sands with gravel, rubble, boulders, and blocks of carbonate rocks and bauxites. The thickness of the deposits at the base of the mogote reaches 50 m.

Two types of bauxite have been distinguished within the area of the deposit based on their mode of occurrence: 1) bauxites in natural occurrences; 2) eluvial-deluvial bauxites - bauxites of deluvial dumps according to B. M. Mikhailov [4].

Bauxites in natural occurrences are confined to the middle subsuite of the Guajaibón suite. The most complete geologic section is revealed in the central part of the mogote (Fig. 4A). Here on the karst surface of light-gray limestones are hard bauxite deposits covered by a terrigenous red colored member consisting of successively alternating gritstones, sandstones, and siltstones up the section. The fragments are represented by quartz, cherts, carbonate rocks and bauxites, and by crystalline glass. The cement is basal contact, consisting of iron clay material. The sorting of the terrigenous deposits is poor; the fragments are generally poorly rounded. The thickness of the member is 10-15 m. Within the eastern part of the mogote the terrigenous red-colored deposits above bauxites are absent

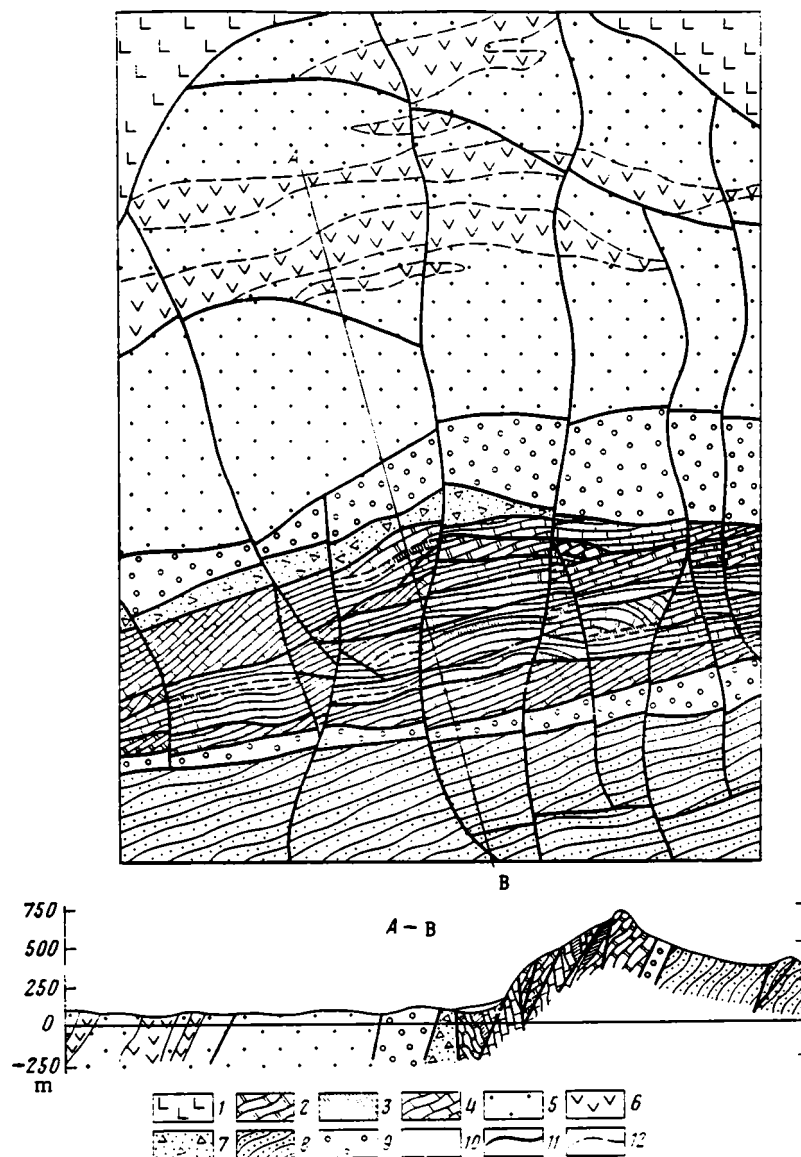


Fig. 2. Schematic representation of the geological structure of the area of the Pan de Guajaibón deposit. 1) Encrucijada suite (K_{1en}) - basalts and lavas; Guajaibón suite (K_{gi}); 2) light-gray limestones and dolomites; 3) red-colored terrigenous deposit - bauxites; 4) Quíñones suite (K_{2qn}) - dark-gray argillaceous limestones; 5) terrigenous carbonate deposits; 6) lavas; 7) Via Blanca suite (K_{2vb}) - siltstones, sandstones, conglomerates; 8) Cacarajicara suite (K_{2ca}) - sandstones, gritstones, conglomerates; 9) Manacas suite (P_{1m}) - olistostrome; 10) Quaternary eluvial-deluvial bauxite formations (only in the section); 11) tectonic displacements; 12) lithologic boundaries.

(Fig. 4B) and, as will be shown later, the quality of the bauxites there is considerably higher. The strike of the bauxite horizon coincides with the general strike direction of the enclosing carbonate rocks ($NE\ 80^\circ$); the predominant dip angles are $50-70^\circ$. The bauxites proper form intermittent lenticular and pocket-shaped bodies, whose thickness varies between 0.5 and 10 m depending on the karst surface of the underlying carbonate deposits. Intense postorogenic tectonic movements have led to the formation in individual blocks of an "inverted" section in which the bauxite horizon is underlain by dark-gray limestones and overlain by light-gray carbonate deposits (see Fig. 4). At the same time there have been signi-

System	Series	Stage	Suite
Quaternary	Recent		Clays, loams loamy sands with gravel, rubble, and boulders of limestones and bauxites
	Upper		
	Middle		
	Lower		
Neogene	Upper (Pliocene)		
	Lower (Miocene)		
Paleogene	Upper (Oligocene)		
	Middle (Eocene)		
	Lower (Paleocene)		Manacas (P ₁ m) 300 m
Cretaceous	Upper	Maastrichtian	Cacarajicara (K ₂ Ca) 600 m
		Campanian	Via Blanca (K ₂ vb) 550 m
		Santonian	
		Coniacian	
		Turonian	
		Cenomanian	Quinones (K ₂ qn) 600 m
	Lower	Albian	Guajai-bon (Kgj) 600 m
		Aptian	Encrucijada (K ₁ en) 800 m
		Barremian	?
		Hauterivian	
		Valanginian	
		Berriasian	

Fig. 3. Stratigraphic classification of the area of the Pan de Guajaibón deposit.

ficant vertical displacements, as a result of which bauxites have been recorded both on the mogote and at its base. Bauxites and terrigenous rocks show signs of tectonic activity, manifested in the form of crush zones, numerous cracks, and slickensides.

Eluvial-deluvial bauxite deposits are developed predominantly near the north slope of the mogote and also fill the tectonic erosion depressions on its surface. At the base of the mogote these deposits extend in a narrow 50-300-m-wide band and occur in the form of a veneer on the karst surface of limestones of the Guajaibón suite. The thickness of the productive layer reaches 35 m, averaging 6-7 m. The section of Quaternary eluvial-deluvial deposits is extremely variegated; however, by general inference, several members (from top to bottom) can be distinguished:

- 1) loams with small fragments of hard, dense bauxites;
- 2) dark-red sandy clays with fragments, boulders, and blocks of hard, dense bauxites 5 mm to 2 m in size;
- 3) multicolored plastic clays with clastic bauxites 5 mm to 40 cm in size;
- 4) multicolored highly plastic clays with manganese nodules and small fragments of carbonate rocks and bauxites.

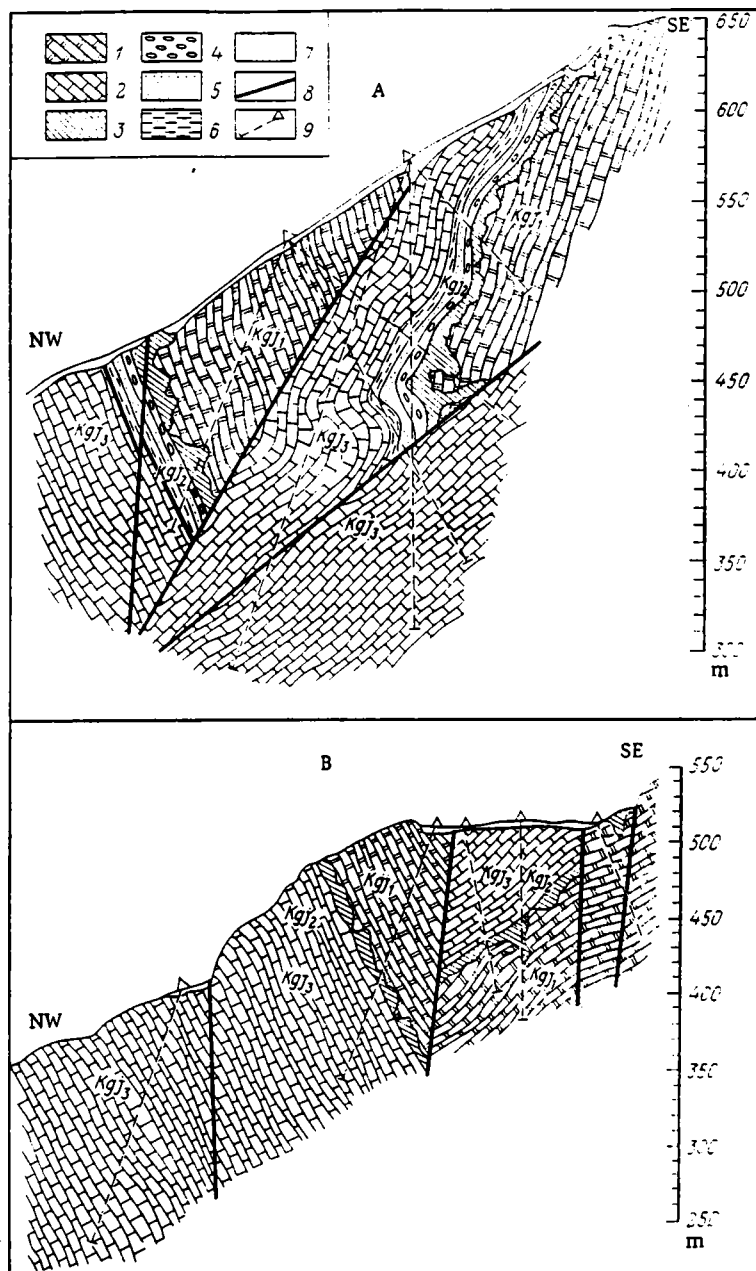


Fig. 4. Geologic sections of the central (A) and eastern (B) parts of the Pan de Guajaibón mogote: 1) light-gray limestones and dolomites; 2) dark-gray argillaceous limestones; 3) bauxites; 4) gritstones; 5) sandstones; 6) siltstones; 7) Quaternary deposits; 8) faults; 9) bore-holes.

The above section of eluvial-deluvial bauxite formations is inferred and discontinuous along the strike direction. Among the productive bauxites are deposits of the second and third members. The content of clastic bauxites in clays averages 10-15% and increase sharply in outcrop areas of bedrock. In these cases accumulations of acute-angled clastic bauxites 1 to 20 cm in size are observed in dark-red sandy clays.

Eluvial-deluvial bauxite deposits on the surface of the mogote are enclosed by areas of tectonic erosion depressions. The thickness of the productive formations is, on average, 2.5-3.0 m. Along the margin of the depressions are traced deluvial dumps of limestone and

bauxite blocks. The bauxite deposits have a higher content of acute-angled fragments of hard bauxite embedded in dark-red sandy clays.

In the section of productive eluvial-deluvial deposits the > 9.5 -mm and partially the 4.75-9.5-mm fractions are strictly bauxitic. The smaller fractions generally correspond to allites.

Chemical Composition of Bauxites. Macroscopically, bauxites are hard, reddish-brown dark cherry-colored rocks of massive, less commonly obscurely bedded structure. The chemical composition was studied by means of traditional methods of petrographic, mineralogical, chemical, thermal, and x-ray diffraction analyses performed at the Center for Geological Research of the Republic of Cuba.

The bauxites consist of oolites and fragments cemented by a finely dispersed pelitic mass composed of hematite, goethite, diaspora, and boehmite with subordinate magnetite, gibbsite, and minerals of the kaolin group. A characteristic feature is the sharp predominance of oolites over detrital material. The pelitic groundmass (matrix) is generally subordinate. There is occasionally a clearly defined orientation of oolites and fragments as well as an overlapping of them by latter small cracks (Fig. 5a).

Oolites of spherical and ovoid forms of concentric structure consist of small (0.01-0.02 mm) grains and microcrystalline aggregates of diaspora, boehmite, hematite, and goethite with subordinate gibbsite, magnetite, and quartz. The diameter of the oolites ranges from fractions of a millimeter to 3 mm. The cavities and pore spaces within these formations are occasionally filled with boehmite and diaspora.

The fragments reach 6 mm in cross section and are essentially poorly rounded. They consist mainly of hematite and goethite with subordinate boehmite and diaspora. Oolites are occasionally found in cavities of the largest fragments.

Cracks 0.05-0.2 mm across separate the oolites and fragments, causing them to be somewhat displaced. They are filled with boehmite, diaspora, and iron minerals, the latter occupying predominantly the central part. The crystal growth of bauxite minerals proceeds from the walls of the cracks toward their axial zone.

The dominant textures of the bauxites are clastic-oolitic (see Fig. 5a) and oolitic (see Fig. 5b). Oolitic veinlets and clastic pelitomorphic particles are less common.

Results of thermal and x-ray diffraction analyses as well as data of mineralogical investigations have shown that diaspora, boehmite, goethite, and hematite are the main minerals. Gibbsite, kaolinite, and halloysite are present in subordinate amounts. Magnetite, quartz, rutile, and anatase occur in the form of impurities.

The chemical composition of bauxites depending on the mode of occurrence and types of deposits is given in Table 1.

Some Problems of Bauxite Genesis. In examining the genesis of diaspora bauxites of Western Cuba, two facts must be kept in mind: 1) the presence of shallow water carbonate sedi-

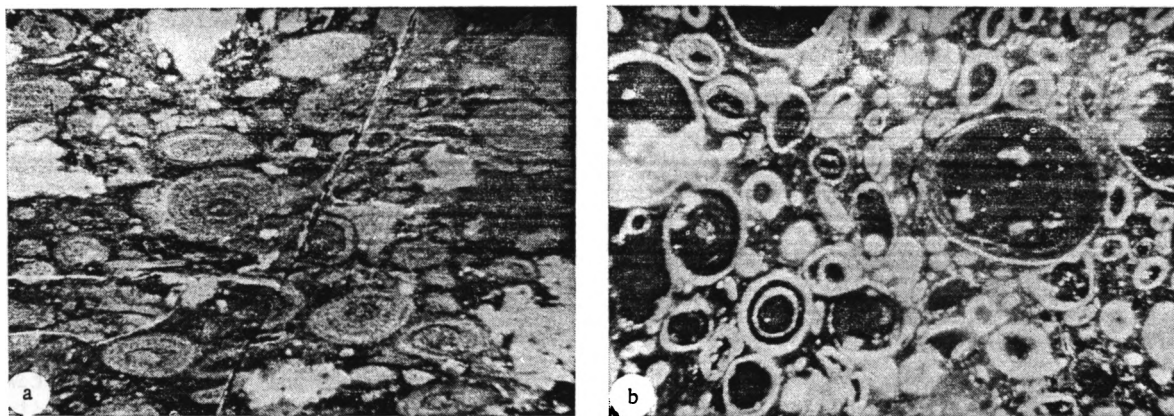


Fig. 5. Textures of diaspora bauxites (a - clastic-oolitic, b - oolitic).

TABLE 1. Chemical Composition of Bauxites

Areas and types of deposits	Av. concn. of major components, % by weight			Silica modulus
	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	
I. Pan de Guajaibón deposit				
Bauxites in natural occurrences:				
a) central part of mogote;	48,57	18,73	18,56	2,6
b) eastern part of mogote	49,54	2,19	30,49	22,6
Eluvial-deluvial bauxites:				
a) fractions > 9,5 mm;	51,17	5,89	28,68	8,7
b) fraction 4,75-9,5 mm	43,20	14,90	23,90	2,9
Eluvial-deluvial bauxites:	36,12	25,09	22,85	1,4
Blocks and boulders of deluvial bauxites	52,53	1,41	30,81	37,2
II. Deluvial bauxites of the Sierra Azul area	57,82	3,50	24,63	16,5
III. Other occurrences of alluvial-deluvial bauxites	52,47—58,67	1,26—3,50	24,00—29,61	15—46

mentation basins, whose deposits systematically crop out; and 2) the proximity of favorable parent rocks as the source of denudation. Here an important role is played by the conditions under which bauxite is preserved from subsequent denudation processes.

It is this geological environment which is characteristic of the formation of bauxites of the Pan de Guajaibón deposit. In Late Albian time, owing to a break in sedimentation and outcropping, carbonate rocks of the lower subsuite of the Guajaibón suite were considerably karstified, and basalts and lavas of the Encrucijada suite were subjected to intense weathering. At the boundary of the Albian and Cenomanian the weathered products were redeposited on the karst surface of light-gray limestones. The difference in the mineral composition of fragments and groundmass (matrix) presumes a fairly high degree of weathering of bauxite parent rocks. Associated with diagenetic differentiation is the formation of oolites which, as noted above, occur also in cavities of the largest fragments. At the same time postsedimentation weathering processes occurred under slightly alkaline or neutral conditions induced slightly alkaline or neutral conditions induced by the enclosing limestones. Weathering was accompanied by the removal of silica and by the relative enrichment of rock in iron oxide, the intensity of which depended on the duration of the process. This is borne out by the difference in the chemical composition of bauxites of the eastern and central parts of the mogote. In the first case the absence of overlying terrigenous deposits predetermined the more prolonged stage of weathering of bauxite formations with the result that the silica concentration here is considerably lower and the iron oxide concentration considerably higher than in bauxites of the central part.

Primary bauxites by analogy with Cenozoic karst bauxites of Cuba and other islands of the Caribbean [1, 3, 5, 8] were presumably plastic clay ocherous deposits of boehmite and gibbsite composition. In Cenomanian time the bauxite deposits were preserved by carbonate rocks of the upper subsuite of the Guajaibón suite. Subsequent catagenesis (according to Strakhov) has led to the compaction of primary soft bauxites and to their transformation into hard, dense rocks. As a result of an increase in temperature and pressure the chemical composition of bauxites was transformed into boehmite and diasporite. A similar process was observed by some investigators for bauxites of the Northern Urals [2].

Regional Paleocene tectonic movements shattered the original deposit into a number of large separate blocks within which occur major horizontal and vertical displacements of the bauxite stratum and enclosing rocks. Eluvial-deluvial bauxite deposits were formed in Quaternary time through partial disintegration of the bed rock of bauxites.

The above genetic model is by no means universally explanatory. Generally, however, it can be used not only for bauxites of the Pan de Guajaibón deposit but also for other regions of Western Cuba, where eluvial-deluvial occurrences of diasporite bauxites have been recorded. It is well to bear in mind that in a specific instance the denudation sources of bauxite material and the carbonate-enclosing rocks may differ.

In conclusion it should be noted that such diasporite bauxites of carbonte formation may be found in certain regions of Central and Eastern Cuba (for example, Sierra de Cubitas, Sierra de Jatibonico, Gibra), where similar geological conditions existed in Cretaceous time.

The possibility exists of a chronological shift of the Albian-Cenomanian bauxite level within the stages of the Cretaceous system, caused by differences in the history of geological development of the western and central parts of the island.

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FACIES AND DISTRIBUTION PATTERNS OF THE MINERAL
RESOURCES OF THE POLTAVA SERIES IN THE DNIEPER-
DONETS DEPRESSION

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UDC 553.492.1(729.1)

The correlations of the facies and tectonic features of the region are investigated, revealing the differences in the facies and mineral resources between the Dnieper-Donets graben and the sides of the depression. The tectonically more active part of the graben is shown to be promising for several important minerals (brown coal, high-grade glass and molding sands, ore placers, etc.). Specific data are given on the stratigraphy of the sediments.

• Various stratigraphic schemes have been suggested for the Poltava series of the Dnieper-Donets depression. In particular, Zosimovich et al. [4] divide it into two suites (Berek and Poltava); Remizov and Berger [6] divide it into five horizons; Romanov [8] into three horizons; and Remizov [7] into three suites (Zmiev, Sivash and Samara). This variation itself indicates the difficulty of correlating the layers of the Poltava series and the wide facies variability of these layers. A study of the facies in comparison with the tectonic features of the region helps understand the territorial distribution of the Poltava layers. We will first describe the main tectonic features of the Dnieper-Donets depression, responsible for the lithogenesis of the Poltava series.

The Dnieper-Donets depression developed along a "syncline-graben-syncline" profile. At the time when it was formed, the Poltava series was a complex syncline with an extremely variable tectonics. The differences were pronounced between the portion superimposed on the Dnieper-Donets graben, with intensive salt tectonics, and the remainder of the area, where salt tectonics was absent. These differences were bound to produce quite different facies in these parts of the depression. This conclusion, drawn from tectonic features, is confirmed by lithological data. The following types of facies are distinguished: 1) widespread brown coal and coaly rocks in the margins of the graben (compared with their almost total absence in the margins of the depression); 2) a much better granulometric uniformity of sand rocks in the graben area, where thick members of same-grade quartz sands are frequent; and 3) relatively less developed sandstones in the sides of the depression as compared with the graben.

Quartz sandstones are also widespread in the Krasnogradsk district, where it is used for local needs. All layers of the Poltava series are subject to facies replacement, but the Zmiev clays less so than any other elements. Sections in bore holes indicating a better facies replacement of Poltava sediments are drawn between the villages Odrynka, Staraya Vodolage, and Prosyanoie [3], in Novaya Vodolage district, and the villages Ogul'tsy, Chere-mushnaya, Litvinovka, and Kobzarevka of Valkovo district, Kharkov province (see Fig. 1).

Another important tectonic feature that affected the lithogenesis of the Poltava series was the widespread presence of depressions (rather than rises) within the graben, responsible for the contrastive paleorelief and the types and distribution of facies. Most of the rises that are marked on the tectonic map of the Dnieper-Donets depression are not expressed in the base of the Poltava series, while the compensatory depressions are distinctly reflected, even though the salt bodies conjugated with them occur at a great depth. The slopes of the depressions are thus not always the slopes of salt domes. The depressions take up most of the territory of the graben.

A gentle dipping of all the layers of the poltava series occurs from the sides to the axis of the basin and from the periphery of the smaller depressions toward the central parts.

Southern Geological Association, Kharkov. Translated from *Litologiya i Poleznye Iskopayemye*, No. 5, pp. 36-43, September-October, 1987. Original article submitted May 27, 1985.

In the direction from the margins to the centers of the depressions, a facies replacement of sediments is observed. The wide spread of the depressions in the graben area was responsible for the predominance of lacustrine, bayou, and palustrine facies, along with estuarine facies. In the sides of the basin, mainly estuarine facies are present but no palustrine sediments are found.

The entire section of Poltava deposits north of Sivash is interpreted as continental sediments, except for some of the Zmiev layers [2, 3]. Further south, these are also probably continental sediments. The main feature of their continental genesis is the facies replacement of the entire section of the Poltava series by coaly rocks. The facies alterations are seen not only in the development of coal but also in a modified granulometry, increased proportion of clay rocks, changed sequence of rock layers in depressions, etc. These alterations are different in depressions of different depths; they also depend on the rate of sinking of the depressions. Rock thickness in shallow depressions (such as Gotval'd) and in the north eastern part of the basin are similar. The normal thickness of the Poltava series ranges from 50 to 60 m. According to Zosimovich [5], near Berek and Taranovka these sediments in the vicinity of the section with Sivash fauna is 60 m. Of this series, the "marine" sediments of the Berek suite take up just 18 m near Berek and 12.5 m near Taranovka, so that the continental segments are thicker than the "marine" layers by a factor of 3 or 4.

In the northeastern side of the basin (Krasnokutsk, Bogodukhov, and other localities), inverse ratios are observed which may be due to the uncertainty of the boundary separating the Berek and Poltava suites. Zosimovich notes that the boundary between the two suites is drawn sometimes along the brown coal, which only occurs in depressions of the graben region, in others along sporadic iron sands and sandstones, and in still others along rare coarse-grained sandstones. There is practically no boundary between the Zmiev and Sivash layers. According to the same data [5], on elevated parts of the bed the Zmiev clays are replaced by a layer of interstratified clays and sandstones or a member of ocherous sand with ferruginous sandstone blocks. Since the Zmiev and Sivash layers have no distinct boundary and the former are replaced in facies on elevated parts, we can refer the Sivash fauna, by way of convention, to the Zmiev layers, assuming that it is characteristic of the lower part of the Poltava series. In addition to the above considerations, one can also mention that the Sivash fauna cannot be "inscribed" into the lithology of the sediments (the facies and the regular alterations of the granulometric composition). The Novoselov glass sands occurring on Zmiev clays are not comparable with Sivash sands, neither lithologically nor by facies.

The Poltava series of the Dnieper-Donets Basin can be subdivided lithologically and by facies into the following strata: sand-clay, sand, sand-siltstone, clay-sand, and clay.

The sand-clay (Zmiev) stratum consists of glauconite-quartz sand and greenish-gray dark-brown-gray clays, sometimes with vegetable remains and brown coal interlayers. The familiar Zmiev flora is confined to these layers; the Sivash mollusk fauna probably belongs to it as well, thus determining the age of the stratum (Late Oligocene).

The Zmiev stratum was formed in the littoral basins of the retreating Kharkov Sea (shallow water marine, littoral-lagoon, and lacustrine-palustrine facies).

These rocks are less exposed or widespread than the overlying sand and sand-silt strata of the Poltava series. They are absent in the right bank of the Oskol River near Kupyansk, Staroverovka, and Shipovatoe, and along the Psel and Vorskla rivers near Lebedin and Lyudzha. Outcrops of the Zmiev stratum are found along the Severnyi Donets near Gotval'd, Uda, Merla, Vorskla, Oleshnya, and other localities. The sediment is 0.5 m thick, with 10-20 m or more in the central parts of the depressions.

The sand (Novoselov) stratum consists of quartzose, mainly small-grained, sometimes medium-grained, sand, locally with rare thin sand and clay interlayers. In the depressions of the Dnieper-Donets graben the sands are humous, coaly, sometimes with brown coal and lignite interlayers. The coaliness is first noticed at the bottom of the section; where the base of the Poltava series is lowered an additional 5-10 m, the entire section is coaly. In Valkov, Novaya Vodolage and Gotval'd districts, coaly material appears starting from the series base elevation of about +100 m.

Besides the monomineral quartz composition, the Novoselov sands are characterized by low contents of the pigment mineral impurities (ilmenite, rutile, etc.), the clay component (locally), and quartz grains smaller than 0.1 mm. They are virtually free of glauconite,

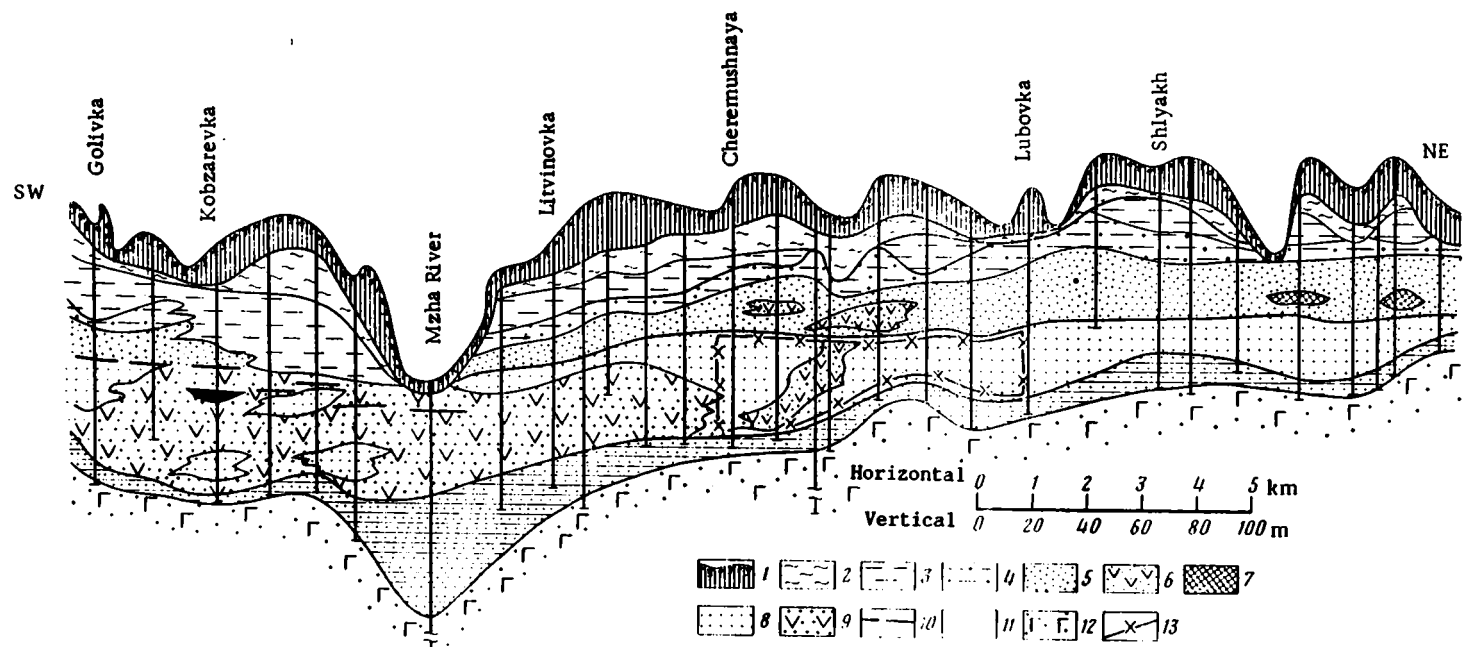


Fig. 1. Geological section of the Poltava series across the margin of the Valkov depression. Overlying sediments: (1) loam (Q); (2) red-brownish clay (N_2^3). Poltava suite (N_{1pt}): (3) variegated clay (Peskov bed); (4) quartzose clayey sand (Prosyantov bed); (5-7) Krasnokut bed [(5) quartzose silty sand, (6) quartzose silty coaly sand, (7) zirconium-titanium placers]; (8-10) Novoselov bed [(8) quartzose small- and medium-grained sand, (9) quartzose small- and medium-grained coaly sand, (10) brown coal]. Berek suite (P_3br): (11) green thin-layer clay with glauconite-quartz sand interlayers (Zmiev bed). Kharkov suite (P_3hr): (12) glauconite-quartz sand; (13) predicted outline of glass sands.

except for single grains in specimens. In some localities these features of sand rocks can be modified due to the appearance of silty and clayey varieties, with a noticeable presence of heavy minerals. Yet, the sand bed is distinctly seen in sections and contains commercial amounts of brown coal and high-grade glass and molding sand. The Novoselov stratum includes layers with trichoptera near Vysokii (Zelenyi Gai), Kiselevka, and other localities and layers with freshwater Miocene fauna at Novopetrovtsy. These sediments can be correlated with the Poltava sections of Donbass that contain Chasov-Yar refractory clays. The contact with the underlying sediments is distinct. The sand stratum is underlain by Zmiev clays or glauconite-quartz sand.

These sediments include the facies of quartz-sand of the midstream parts of plainland riverbeds and the facies of quartz-sand-clay sediments of bayous of plainland rivers. This is confirmed by oblique stratification, relatively larger sand grains, the position in the section (beneath the estuarine shoal facies), traits of a continental genesis (the presence of coal, etc.), and the dynamic granulometric diagrams, compiled by Romanov [8].

In depressions of the graben, the Novoselov stratum consists mainly of quartz-sand vegetable-detrital facies of bayou sediments and widened river beds, and the facies of lakes and peat bogs.

The Novoselov sediments are found on a much wider area than the underlying Zmiev stratum; they are observed in outcrops along the Ol'khovatka, Mzha, Berestovaya, Orchik, Merla, Vorskla, Psel, and Severnyi Donets rivers and their tributaries near Novoselovka, Cheremushnaya, Berestoven'ki, Okhochee, Lyudzha, Staroverovka, and other villages. In the northern side of the basin the sediments are 15-20 m thick, in the graben on the slopes of the depressions 30, and in the central parts up to 50 m and more.

The sand-silt (Krasnokut) stratum consists of quartzose silty sand, sandy siltstone, and marshallites, often with kaolin, locally with thin rare interlayers of sandstone and quartzose small- and medium-grained sand. In the depressions of the graben these are coaly sediments, sometimes with brown coal interlayers. This part of the Poltava series contains minable zirconium-titanium placers and very fine thin and dustlike molding sands.

The Krasnokut stratum is represented by the facies of quartz-sand metalliferous sediments of river shoals and beaches, as confirmed by thin diagonal and very small wavy stratification of "basketlike" rocks, its position in the section (above the midstream facies), and a smaller grain size compared with the subjacent beds. In graben depressions, the facies of quartz-sand metalliferous sediments of shallow lakes and beaches and the facies of quartz-sand sediments of stagnating lakes and peat bogs are mainly observed. A part of the Krasnokut stratum consists apparently of aeolian and aquatic-aeolian formations.

The upper and lower contacts of this stratum are distinct. The succession of the granulometries can be seen by the naked eye. The Krasnokut sediments are widespread and seen in exposure in the basins of the Northern Donets, Merla, Vorskla, and Psel Rivers near Krasnokut, Kharkov, Novaya Odessa, Kozievka, Lyudzha, Mikhailovka, Novoselovka, Novaya Sech', and other localities. The sediments in the northern side of the Dnieper-Donets Basin are 10 m thick, on depression slopes 20, and in central parts 40 m thick and more.

The clay-sand (Prosinov) bed consists of quartzose inequigranular clay-kaolinic sands, locally with interlayers of quartzose ferruginous sandstones, rarely with sandy clays. On high watersheds the quartz sands at the top of this section are often cemented to kaolinic sandstone. In the graben depressions these rocks are replaced facially by variegated clays and sand-coaly rocks (facies of lakes and peat bogs). The Prosinov stratum is comprised of the facies of clay-quartz-sand sediments of estuarine bars, near-river flood valley zones, and clayey and quartz-sandy sediments of flood valley lakes. The bed contains productive clayey placers of molding sands and, partly, construction sands.

The sediments of the Prosinov bed are less widespread and eroded on a large area. They are exposed along the Ol'khovatka, Berek, Berestoven'ka, Orchik, Merla, and other rivers. The sediments are 4-10 m thick (up to 20 m in the depression slopes).

We have placed with the Poltava series a bed of (Peskov) variegated clays that includes the Poltava alluvial suite and represents the facies of clayey sediments of inner zones of river flood valleys and crusts of weathering. The variegated clays occur in highest watersheds; they are 0.1-5 m thick (up to 25 m thick in graben depressions). The nearby Pliocene

terraces display a similar build (flood valley alluvium at the bottom and flood valley variegated clays at the top).

In deep depressions of the area of salt tectonics, the Poltava series exhibits an anomalous section, with sulfate-carbonate rocks and diatomites appearing locally. The sediments of these depressions that cover small areas represent mainly lake and marsh facies.

A comparison of our stratigraphic scheme of the Poltava series with that of Zosimovich and other investigators, approved by the International Crystallographic Union in 1964 and used in geologic surveys, indicates that our scheme of lithological subdivision of Poltava sediments is consistent with the scheme of their divisions, suite-by-suite. As mentioned earlier, Zosimovich does not draw any distinct boundary between Berek and Poltava suites; as a result, the volume of the Berek suite in the northeastern side of the basin (near Krasnokut, Bogodukhov, and other localities) is increased drastically. In the monograph [5] little factual data are given on lithology (there are no lithologic sections across the basin; the granulometric composition is given only for three sites in one depression, etc.). No stratigraphic description of mineral deposits is offered. Since the Poltava beds are poor in paleontologic remains, the lithology of the sediments should be studied much more carefully to resolve the controversial aspects of their stratigraphy.

The regularities of the occurrence of minerals in the Poltava suite are connected with stratigraphic, lithologic, tectonic, and geomorphologic features of the territory. The stratigraphic regularity is characterized by the confinement of certain minerals to the subdivisions of the Poltava series as identified by us. The variation in the granulometric composition of the sediments is consistent with these regularities as well as with lithologic-facies and structural-tectonic patterns. Coarser grains (small- and medium-grained sediments) are associated with the Novoselov stratum but not with the periphery of the Poltava marine basin [8]. Since the Novoselov stratum is represented by specific facies and the facies are affected by tectonics, all these regularities are interconnected. The relatively coarser grains are more widespread in the graben region. Thick members of homogeneous sands and well washed-off clays are found there in abundance (Table 1). The influence of the salt tectonics in the graben area was a factor in shaping the contrastive paleorelief conducive to the sharp differentiation of hydrodynamic regimes in the lakes and river basins, which left distinct marks of an intensive activity in some locations. This also explains the confinement of most zirconium-titanium placers to depression slopes. For example, the Lebedin placer is located in a slope of a depression (compensation trough) associated with the formation of the Sinev salt stock; the Krasnokut and Novaya Vodolaga placers are associated with depression slopes connected with Karaikoz, Kolontai, and Valkovo salt stocks, etc. No noteworthy placers have been found in the central parts of the depressions.

The essence of the lithologic-facies regularity is the fact that the minerals of the Poltava series are associated with specific facies and zones of facies replacement of sediments. Zirconium-titanium placers represent the facies of shallow lakes, lake and river beaches, and flood valley shoals. A facies transition of coal-free metalliferous quartzose silty sands to coaly sands with brown coal lenses is observed in some locations (Novaya Vodolaga placers).

Glass sands belong to the facies of quartz-sand vegetable-detrital sediments of midstream and near-midstream parts of widened plainland riverbeds and normal riverbeds, and possibly lakes.

The structural-tectonic regularity consists of the fact that minerals are found in certain structural parts of the Dnieper-Donets depression. Thus, high-grade glass sands are common in the graben region, where they occur not everywhere but with a tendency toward slopes (margins) of the depressions. As noted, the sands here have a better granulometric uniformity and contain coaly matter [3]. The probability of placers of such sands in the sides of the basin is very low. Brown coal deposits are found only in graben depressions. Most zirconium-titanium placers are confined to depression slopes.

The geomorphologic regularity is determined by the constancy of the altitudes of productive horizons around depressions and along the northeastern side of the Dnieper-Donets Basin, as opposed to their variability across these structures. Thus, the roof of the high-grade glass sand near Novoselov, Prosyano, Novaya Vodolaga, Cheremushnaya, Berestoven'ka, and Okhochee Villages lies at elevations of +128 and +133 m, less often slightly higher

TABLE 1. Results of Analysis of Quartz Sands, Poltava Series

Site of sampling (hole number)	Bed	Sampling interval, m	Chemical composition, %					Mechanical composition (%) by fractions, mm				
			SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	TiO ₂	calcin. loss	>0.8	0.8-0.5	0.5-0.25	0.25-0.1	<0.1
Novoselovka, Dnieper graben area (10)	Krasnokut	24,7-26,0	Not det'd	0,13	Not det'd	Not det'd	Not det'd	0	0	0,21	37,67	62,12
		26,0-27,15	»	0,08	»	»	»	0	0	5,85	33,65	60,50
	Novoselovka	27,15-28,20	»	0,04	»	»	»	0	2,13	44,07	51,94	1,86
		28,20-29,75	»	0,04	»	»	»	0	0,37	33,07	65,79	0,77
Cheremushnaya, Dni- eper graben area (136)	»	32,0-33,0	99,49	0,01	0,13	0,01	0,08	0,2	6,1	61,5	30,6	1,6
		33,0-34,0	99,5	0,01	0,16	0,01	0,10	0,5	9,9	50,7	37,2	1,7
		34,0-35,0	99,3	0,01	0,10	0,02	0,21	0,3	6,1	37,3	53,9	2,4
Lyudzha, northeastern side of the Dnieper- Donets Basin (52)	Krasnokut	18,0-19,5	93,68	0,39	3,66	0,75	1,27	0	0,07	0,09	0,57	99,27
		19,5-21,0	97,29	0,18	1,57	0,27	0,95	3,09	5,49	2,37	42,72	46,33
	Novoselovka	25,5-27,0	99,21	0,10	0,40	0,02	0,17	1,40	10,67	64,75	21,68	1,50

(Okhochee). Toward the depression centers the roof layers of sands are lower, but they become heavily coalified sands rather than glass sands in those locations.

As one moves further from the graben toward the Voronezh anticline, the roof and base of the productive beds of the Poltava series occur at higher elevations. Since these elevations are quite close to the present topographic surfaces, erosional wedging of Poltava sediments is observed in this direction at some distance from the graben [1, 3]. The placers also comply with a geomorphologic regularity, so that an analysis of the elevations of present topographic surfaces and the thicknesses of suprajacent sediments makes it possible to reject those parts with eroded productive horizons and select the optimal areas for reconnaissance.

* * *

The Poltava series of the Dnieper-Donets Basin is subdivided according to its lithological characteristics into the following beds (bottom to top): sand-clay (Zmiev), sand (Novoselov), sand-silt (Krasnokut), clay-sand (Prosinov), and clay be (Peskov).

The age of the Poltava series ranges from the Late Oligocene to the Miocene. The boundary between the Oligocene and the Miocene is drawn along the base of the Novoselov bed. The Poltava sediments are represented by continental facies, except for some of the Zmiev layers.

The occurrence patterns of minerals in the Poltava series are determined by the stratigraphy and lithology of sediments and the tectonics and geomorphology of the territory. Brown coals are found only near the Dnieper graben. High-grade glass sands are confined to the Novoselov bed in the graben area. They tend to occur in the slopes of compensation depressions. The quartz sands of this territory also exhibit a better granulometric uniformity and are often flushed of clay and are promising as high-grade molding materials. Zirconium-titanium placers are associated with the Krasnokutsk bed and also tend to occur in depression slopes, although in small concentrations they are also found elsewhere.

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TERRIGENOUS-MINERAL ASSOCIATIONS IN THE JURASSIC DEPOSITS OF TIEN SHAN

I. I. Bedeshev

UDC 552.181:551.762(235.216)

The author has delineated terrigenomineralogical subdivisions of the Ferghana and Eastern Ferghana basin during Jurassic times by studying of the material compositions of the deposits. He established the sources of drift and traces their evolution through time and space.

In our conception, Southern Tien Shan includes Central Tadzhikistan, Ferghana, and the Eastern Ferghana basin. The Jurassic deposits of the above-mentioned regions have long attracted the interest of geologists, since many sedimentary deposits of industrial minerals, among which coal, oil, gas, and placers are of prime importance, are associated with them. Present research on characterizing the deposits in the region under consideration is concerned both with general and specific problems of the stratigraphy and tectonics [1, 2, 4, 18, 20, 21, 24, 25, 31]. Data on the material composition is extremely limited. The most complete investigations have been carried out by V. A. Babadarly and A. Dzhumangulov [3]. However, these investigators restricted themselves primarily to describing of the composition of the terrigenous minerals and did not pursue questions concerning the genesis of the mineral associations or their connection with the sources of drift [3].

The author faced the problem of establishing the ancient distributive provinces, the direction of drift, the manners of transport of the fragmental material, and also the evolution in the composition of the distributive provinces and sedimentary basins through space and time on the basis of a lithofacies and mineralogical-petrographic study of the Jurassic deposits. The solutions to these problems have both theoretical and practical significance.

The results of investigations of the Jurassic deposits of Central Tadzhikistan, Ferghana, and the Eastern Ferghana basin are presented in the present article. These investigations are part of a complex of investigations aimed at clarifying the Jurassic history associated with the geological evolution of southeast Central Asia which were carried out by coworkers of the Laboratory of Sedimentary Formations of the Geological Institute of the Academy of Sciences of the USSR under the direction of the Academician of the Academy of Sciences of the USSR R. P. Timofeev.

The Jurassic deposits of Central Tadzhikistan fill contemporary Mesozoic basins which, at the present time, lie among Paleozoic rocks in the form of tectonic sheets. The Fan-Yagnobsk, Kshtut-Zauransk, and Shing-Magiansk are the largest among them. They are relicts of a large, unified, intermontane basin which stretched from east to west between the ancient rises of Gissar and Turkestan (Fig. 1).

Within Eastern Ferghana, the deposits of Jurassic age have a submeridional strike and can be traced from the Kubmel' deposits in the north to the Kunsaisk region (KNR) in the south. They make up the present Eastern Ferghana Range. Finally, they are exposed within the Ferghana depression along its mountainous framework. To the side of the basin's central portion, deposits of Jurassic age are buried under Upper Mesozoic-Cenozoic formations, where (according to geological data), they occur at depths of 10,000 m or more (Fig. 1).

From the tectonic point of view, the basins under investigation coincide with the Ural-Tien-Shan orogenic (deutrogenic) belt [10, 28].

Lithologically, the Jurassic deposits are represented by conglomerates, gravelites, sandstones, siltstones, claystones, carbonaceous claystones, and coal. From the genetic point

Institute of Geology, Academy of Sciences of the USSR, Moscow. Translated from *Litologiya i Poleznye Iskopaemye*, No. 5, pp. 44-57, September-October, 1987. Original article submitted May 14, 1986.

(Okhoochee). Toward the depression centers the roof layers of sands are lower, but they become heavily coalified sands rather than glass sands in those locations.

As one moves further from the graben toward the Voronezh anticline, the roof and base of the productive beds of the Poltava series occur at higher elevations. Since these elevations are quite close to the present topographic surfaces, erosional wedging of Poltava sediments is observed in this direction at some distance from the graben [1, 3]. The placers also comply with a geomorphologic regularity, so that an analysis of the elevations of present topographic surfaces and the thicknesses of suprajacent sediments makes it possible to reject those parts with eroded productive horizons and select the optimal areas for reconnaissance.

* * *

The Poltava series of the Dnieper-Donets Basin is subdivided according to its lithological characteristics into the following beds (bottom to top): sand-clay (Zmiev), sand (Novoselov), sand-silt (Krasnokut), clay-sand (Prosinov), and clay be (Peskov).

The age of the Poltava series ranges from the Late Oligocene to the Miocene. The boundary between the Oligocene and the Miocene is drawn along the base of the Novoselov bed. The Poltava sediments are represented by continental facies, except for some of the Zmiev layers.

The occurrence patterns of minerals in the Poltava series are determined by the stratigraphy and lithology of sediments and the tectonics and geomorphology of the territory. Brown coals are found only near the Dnieper graben. High-grade glass sands are confined to the Novoselov bed in the graben area. They tend to occur in the slopes of compensation depressions. The quartz sands of this territory also exhibit a better granulometric uniformity and are often flushed of clay and are promising as high-grade molding materials. Zirconium-titanium placers are associated with the Krasnokutsk bed and also tend to occur in depression slopes, although in small concentrations they are also found elsewhere.

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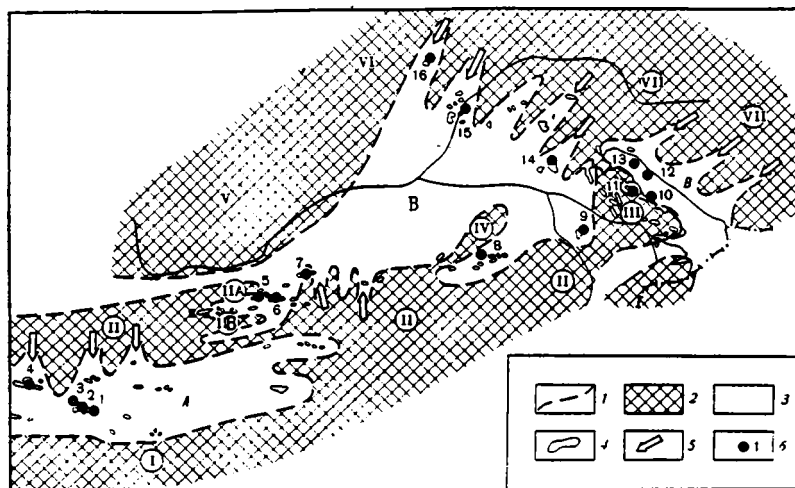


Fig. 1. Paleomorphostructural map of the Jurassic relief. 1) approximate contours of the paleo-rises; 2) principal paleo-rises (I: paleo-Gissar, II: paleo-Turkestan, III: Yassinsk paleo-water-divide, IV: paleo-Karachaty, V: paleo-Chatkal, VI: paleo-Kuramin, VII: paleo-Narynsk land); 3) Jurassic sedimentary basin (A: paleo-Zeravshansk, B: paleo-Ferghana, C: paleo-Eastern-Ferghana); 4) present contours of outcrops of Jurassic deposits; 5) principal directions of drift of terrigenous material; 6) exposures studied; 1) Ravat, 2) Ravat-1, 3) Dzizhikrut, 4) Shing-Magian, 5) Shurab, 6) Samarkandek, 7) Guzan, 8) Kizyl-Kiya, 9) Irisu (Allyar), 10) Karashura, 11) Beshterek, 12) Kok-Kiya, 13) Tuyuk, 14) Markai, 15) Tash-Kumyr, 16) Arkit.

of view, they are a complex consisting of alternating alluvial, lacustrine-marsh, and lacustrine deposits. The regular alteration of the genetic types of deposits enumerated above resulted in the formation of the elementary cycles and morphological variations. Two groups of elementary cycles can be distinguished alluvial-lacustrine-marsh. Depending upon the character of the alluvium (mountain, mountain-plain, or plain), diverse morphological variations can be distinguished. A detailed lithofacies and mineralogical-petrographic investigation of the Jurassic deposits of both the given region and the adjoining territories, one which takes into consideration the changes in the character of the elementary cycles and their morphological variations allows us to clearly distinguish three episodes corresponding to macrocycles (subformations), each of which corresponds to a large-scale stage in the evolution of the region and each of which is characterized by a particular time interval. The macrocycle can be distinguished from one another by group compositions of plant associations [1, 2], climate, character of the environment for sediment and coal deposition, material composition, and other specific indications.

The first macrocycle corresponds to the Lower Jurassic (Aalenian), the second to the Bajocian-Bathonian, and the third to the Callovian. Deposits of the Oxfordian, Kimmeridgian, and Tithonian are absent in these basins. The formation of the deposits of the first and second macrocycles occurred under humid conditions, and some change in climate toward aridization took place during the formation of the deposits of the third macrocycle; the rocks took on a reddish coloration in connection with this change.

The classification of V. D. Shutov [32] was used when identifying the mineral associations. As a result of studies of sections of the three macrocycles, differences in their material composition were established and terrigenous-mineral associations were identified as characteristic of individual areas in the region under consideration. These areas differ from one another with respect to quantitative ratios of rock-forming components (quartz, feldspars, and rock fragments) and also with respect to their morphological features. When studying the fragmental quartz, we used the classification scheme of A. G. Kossovskaya and took into account the assumptions made in previous reports [16, 17]. The genetic aspects associated with the investigation of different morphological varieties of quartz were re-

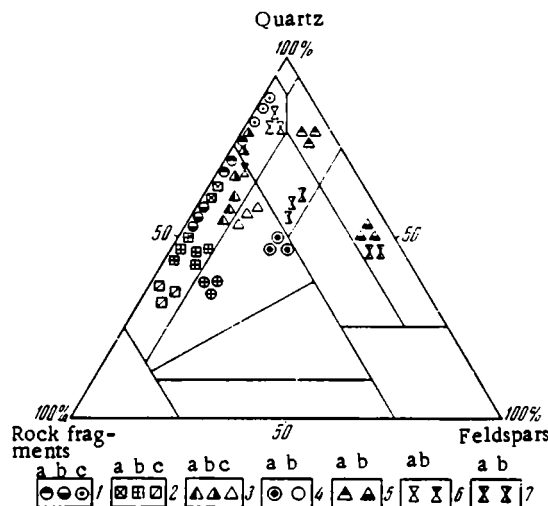


Fig. 2. Material composition of Jurassic sandy-gravelly rocks of Tien Shan: 1) Zerabshansk basin; 2-5) Ferghana basin (2: Southern border, 3) eastern 4) northeastern, 5) northern); 6-7) Eastern Ferghana basin (6, Kok-Kiya, Tuyuk, 7) Beshterek, Karashura); a) sandstones and gravellites of the first macrocycle; b) of the second; c) of the third.

flected in these reports most clearly. The investigations of the peculiarities of the minerals in the light and heavy fractions and also the primary clay cement had the most importance for establishing the regions of drift.

The analysis of the material composition of the sandy-gravelly rocks allowed us to distinguish 17 terrigenous-mineral associations among the deposits of Jurassic age. Individual associations were connected with one another by gradual transitions, others changed very abruptly. Their material compositions are presented in a diagram (Fig. 2).

Zeravshansk basin (Central Tadzhikistan)

Three associations formed in the Jurassic deposits of Central Tadzhikistan: siliclastic-quartzitic, oligomictic-quartzitic, and quartz-graywacke (Fig. 2).

The siliclastic-quartzitic association is characterized by conglomerates and gravellites of alluvial origin from the first macrocycle at the Dzhizhikrut, Ravat, and Pasrud sections. Elevated concentrations of quartz, which range from 80 to 90%, are characteristic. The quartz is represented by two morphological varieties: sedimentational (redeposited) and effusive. The first type is the most common. The second type of quartz is present in the form of individual grains. The content of rock fragments is small and varies from 10 to 20%. Fine-grained siliceous and quartzic-micaceous shales are found among them. As a rule, they are slightly rounded. Fragments of effusives are very rarely encountered. Zircon, tourmaline, garnet, rutile, and ilmenite are among the accessory minerals present. The zircon and tourmaline are rounded and semi-rounded varieties. Kaolinite and hydromica of the $2M_1$ polymorphic modification, derived from weathering of the surrounding crust, are among the clay minerals present. Chlorite is present in trace amounts.

An oligomictic-quartzitic association was established in the alluvial and lacustrine-marsh deposits of the second macrocycle. It is characterized by a 70-80% quartz content and up to 25-30% rock fragments. Fragments of silty-clayey and clayey shales enriched in organic material occur alongside the above-mentioned type of fragments in this association.

Organic material is present in the form of irregular clusters, veins, or thin disseminations throughout the entire rock. It is usually devoid of primary structure, but sometimes fine plant detritus can be successfully distinguished in individual rock fragments. The texture of the silty-clayey and clayey rocks is shaly, more rarely structureless: the degree of rounding of grains is varied, but semirounded forms predominate. The accessory minerals are

represented by rounded and semirounded grains of zircon, tourmaline, and rutile. Pyrite in the form of irregular grains and concretions, usually associated with iron hydroxides, are among the authigenic minerals present. The clay minerals are represented by kaolinite and hydromica.

A quartz-graywacke association was established in the alluvial sediments of the third macrocycle within the same section.

In contrast to the preceding associations, it is distinguished by a high concentration of rock fragments (up to 40%) and a decrease in quartz content (a decrease of up to 55%). Opalized grains of bipyramidal shape, with corroded, filled-in edges, occur among the quartz grains along with the reworked variety. Feldspars may be present in small quantities in a given deposit (up to 5%). Grains of plagioclase occur among these, together with the potassic varieties of feldspar. The rock fragments are analogous in composition to the association mentioned above, but include fragments of effusive rock. The accessory minerals are zircon, rutile, and tourmaline. In addition, grains of ilmenite, sphene, and epidote can be found. The clay minerals are more diverse, including chlorite and mixed-layered formations of hydromicaceous-montmorillonitic composition along with hydromica. Kaolinite is found only in individual samples, where its concentrations are very small.

Possible Source Rocks

The analysis of the composition of the fragmental material gives a reason to believe that the most probable source rocks for the formation of the associations mentioned above were Paleozoic sedimentary (silty-clayey, siliceous-clayey, and other rocks) and effusive complexes located within the paleo-Turkestan Rise. In this case, it should be especially emphasized that neither the petrographic composition nor the paleogeography of the areas eroded remained constant through space and time.

In particular, the rocks of the Upper Paleozoic formations, represented by an alternation of varied siliceous, silty-clayey, carbonate-siliceous, and quartzitic-micaceous shales along with jasper and a different type of sedimentary formation (from carbonaceous siltstones and claystones to sandstones) all of which are analogous in material composition to the established mineral associations [30], should be, by all appearances, the complex we are looking for.

The high concentration of quartz in the composition of the first association and the presence of stable mineral varieties (zircon, tourmaline, and rutile) among the accessory minerals is connected with the fact that rocks of the complex indicated above (characterized by significant weathering) did experience erosion.

During the formation of the second association, primarily individual horizons of sedimentary complexes consisting of alternations of siltstones, claystones, carbonaceous siltstones, and fine-grained sandstones were involved within the denudation zone. A similar rock complex exists at the present time in the composition of the Upper Paleozoic flyschoid formation, where it forms individual bands of 100- to 140-m thickness. At the present time, it sporadically outcrops in the territory of the Turkestan Range. It can be suggested that it was widely occurring within the paleo-Turkestan Rise in the past.

Fragments of effusive rocks and grains of effusive quartz appear in the composition of the third association, together with fragments of sedimentary-metamorphic rock widely represented within the mineral association. Apparently, this is connected with several changes which took place in the sources of drift. Deposits enriched in fragments of effusive rocks were included among the latter in the region of denudation. By all appearances, they were an Upper Paleozoic flyschoid complex of the following composition: 40-60% quartz; 10-20% feldspars; and 15-20% fragments of effusive rocks [30]. At the present time, the complex occurs along the northern border of the basin, within the Mechetli structure. This is also confirmed by the composition of the accessory minerals of the third association and the composition of the sedimentary complex described above. The latter were represented by zircon, tourmaline, sphene, epidote, and other minerals.

Consequently, the source of drift during the formation of the mineral associations in the sections of the paleo-Zeravshan Basin was primarily a siliceous-terrigenous flyschoid formation of Paleozoic age with a mineral composition, as noted above, analogous to the composition of the mineral associations. In addition, rocks of the same age and enriched in fragments of effusives of alkaline composition were periodically involved in the region of

sediment accumulation. The indicated complexes were widely distributed within the paleo-Turkestan and, in particular, within the paleo-Gissar rises. They are widely occurring at the present time. It is interesting that there is an absence of erosion products from granitoid massifs in the composition of the Jurassic deposits of the paleo-Zeravshansk basin located to the north, deposits which enjoying widespread occurrence within the paleo-Gissar. Ancient rivers to the south removed all of the terrigenous material to the side of the Afgan-Tadzhiksk sedimentary basin. At the present time, erosion products of the Gissar intrusive complexes have been identified in all of the sections located on the southwestern and southern slopes of the Gissar Range [6, 7].

This situation has been attributed to a number of causes, the most objective of these being, in our opinion, the following. The first involves the absence of decomposition products of granitoid massifs in the Jurassic sections of the paleo-Zeravshansk basin due to the absence of an ancient river network on the northern slopes of the Gissar paleo-rise. The latter apparently were characterized by limited leveling. Woody vegetation grew on these slopes from the Lower to the Middle Jurassic inclusively. This was probably the main factor preventing the formation of a river network. The presence of small lacustrine and lacustrine marsh basins in deposits with practically no sediments of alluvial origin confirmation this. The Ziddy, where the complete section of Jurassic deposits amounts to all of 80-90 m at the same time that the thickness of Jurassic deposits reaches 900 m in the central area of the paleo-Zeravshansk basin, can serve as an example of such a lacustrine basin.

The second cause was that the original dimensions of the paleo-Gissar were significantly wider than those indicated on any existing paleogeographic maps (Fig. 2) [6, 27, 28]. Accordingly, the rivers draining the paleo-Gissar did not encroach upon the granitoid massifs; they eroded Paleozoic sedimentary complexes which were apparently situated along the northern slope of the paleo-Gissar.

The Ferghana Basin

A number of regions differing in material composition of their mineral associations can be distinguished within the composition of the Jurassic deposits of the Ferghana Basin. These differences are primarily due to the petrographic background of the eroded areas. Brief descriptions by region are given below.

The Jurassic Border of the Basin. Four mineral associations were established in the Jurassic deposits of this region (Fig. 2): three associations coincided with sections of the Surab, Samarkandek, and Guzan and one coincided with a section of the Irisu (Allyar).

An oligomictic-quartzic association was established in the deposits of the first macrocycle over the entire area of the Jurassic Ferghana. It is distinguished by a high content of quartz (reaching 75%) in which grains of isometric shape with wavy extinction predominate and zircon, tourmaline, and apatite (60-70%) are included. Metamorphic quartz occupies second place (15-20%). The concentration of sedimentary-sedimentational quartz does not exceed 10%. The fragments consist of the following rock groups: siliceous, quartzic-micaceous, clayey, and silty-clayey shales. Their concentrations reach 35%. The siliceous fragments consist of a finely aggregated chalcedony mass with barely significant, thin layering which is due to the presence of disseminated organic matter. In many fragments, rounded inclusions of radial or aggregate-polarized chalcedony formed from radiolarian remains are present. Similar formations have been classified as phtanite by A. G. Kossovskaya [17]. With increasing concentrations of clayey material, they grade into clayey phtanites [33]. These types of rock fragments are especially abundant in sections of the Southern Ferghana. Silty-clayey and clayey fragments are constant components among the durable rock fragments of the Jurassic deposits on the mountainous rim of the Ferghana depression. Fragments of effusive rocks are rare; they are found in the form of separate, isolated grains. The most abundant of the accessory mineral are ore minerals: magnetite, ilmenite, and also zircon, garnet, sphene, and leucoxene. Micaceous minerals are represented by brown and greenish-brown biotite and muscovite. Clay minerals encountered included kaolinite and hydromica. The authigenic mineral are represented by pyrite and siderite.

An oligomictic-quartzic association with a high content of rock fragments is abundant in the deposits of the second macrocycle. It resembles the first association in material composition. A high concentration of fragments of sedimentary rock, in which siltstones, monomictic sandstones, and clayey shales predominate, are a characteristic feature. The proportion of such fragments can fall to 70% of the total concentration of rock fragments.

Their quantity in this association is 40-50%, i.e., as much as the quantity of quartz. As in all of the associations described above, feldspars are not present. Among the accessory minerals, zircon, garnet, or, more rarely, tourmaline are characteristic; magnetite and ilmenite are also encountered. The clay minerals are represented by ilmenite and kaolinite.

A quartz-graywacke association is characteristic of the lacustrine and alluvial deposits of the third macrocycle in the Shurab, Samarkandek, and Guzan sections. The presence of quartz (30-40%), rock fragments (50-60%), and feldspars (0-10%) is characteristic of this association. The concentration of siliceous shales, for which spherical shapes of 0.02-0.1-mm dimensions represented by chalcedony are characteristic, seldomly shows an increase among the rock fragments. Apparently, a large portion of these shales are the remains of radiolarians. In addition, fragments of clayey and silty-clayey shales and monomictic sandstones in an intermediate stage of metamorphism can be found. Among the accessory minerals, zircon, hematite, magnetite, ilmenite, and small quantities of sphene and garnet are present.

Hydromica, montmorillonite, chloride, and a mixed-layer phase of a hydromica-montmorillonitic composition are the most abundant of the clay minerals. Kaolinite is present as an admixture.

A quartz-graywacke association with a high content of effusive-rock fragments was established in the deposits of the third macrocycle in the sections of Irisu (Allyar). The concentrations of rock fragments and quartz in the association are practically identical (quartz amounts to 50%, and rock fragments constitute up to 45%). Feldspars are present in insignificant quantities. They amount to no more than 5%. Grains of pure quartz without inclusions or with sparse, usually linearly oriented, almost imperceptible gas-liquid inclusions derived from the breakdown of effusive rocks predominate among the quartz. In addition, veined and sedimentary-sedimentational quartz can be found. The rock fragments are mainly represented by acidic and basic effusives. Siliceous shales are present in small quantities.

Zircon and tourmaline are the most abundant accessory minerals. Anatase, brookite, epidote, apatite, and pyrite are present in small quantities. This association can be distinguished by high concentrations of hematite-limonite, magnetite, ilmenite, and leucoxene.

Pyrite and barite are among the authigenic minerals. The clay minerals are represented by chlorite and hydromica; kaolinite is present in the form of an admixture.

As was noted above, the mineral associations delineated in the Jurassic section of Southern Ferghana are characterized by relatively high levels of persistence over the area.

The analysis of the compositions of the mineral associations with the material composition of the drift region led us to the conclusion that the probable source rocks were various sedimentary-metamorphic and effusive-sedimentary formations with petrographic compositions similar to those of the mineral associations.

In particular, the most probable source of drift during the formation of the first association was primarily various sedimentary rocks (siliceous, clayey-siliceous, quartz-sericitic, shales, and others). Among the Paleozoic formations, a thick stratum consisting of an alternation of siltstones, claystones, siliceous and siliceous-clayey shales with compositions identical to those of the first association is well known. At the present time, these rocks can be traced in the form of a narrow band within the Turkestan Range [23].

The high content of rock fragments in the composition of the first association is interesting; this is not very characteristic of the deposits of the first macrocycle; it is not characteristic within the given region or in the entirety of Central Asia for that matter. As a rule, the sediments of the first macrocycle are enriched in quartz, i.e., they are characterized by a monomictic nature. The quartz concentration reaches 95% in number of cases [6, 7, 28]. This apparently connected with the fact that relatively fresh rock was subjected to erosion within this region. The lithofacies and paleogeographic investigations showed that individual areas in the territory of Southern Ferghana experienced a fairly active tectonic life during pre-Jurassic times, this impeded the formation of weathered horizons.

The second formation can be distinguished from the formation described above by a high content of rock fragments with silty-clayey, clayey carbonate shales, and sandstones predominating. This is apparently due to the fact that chiefly sedimentary formations represented by clayey shales, siltstones, claystones, and sandstones were involved during the formation of the second mineral association within the region of sediment accumulation, i.e.,

a sandy-clayey sedimentary complex was eroded during this time. The Silurian formations which occur in the region of the Turkestan Range [23] may be a similar complex. Their identical compositions are an eloquent indication of this.

The third association can be distinguished from the two preceding ones by its high (up to 60%) content of rock fragments, among which siliceous shales predominate. This abrupt change in the material composition of the third association is connected with a change in character of the sources of drift to sources where rocks characterized by high concentrations of siliceous varieties were abundant. These rocks may have been Upper Paleozoic formations with high concentrations of siliceous rocks enriched with spicules of siliceous sponges and tests of radiolarians [30].

In the sections of Irisu (Allyar), the third association becomes more of a graywacke association on account of a sharp increase in effusive-rock fragments. In composition, these rocks correspond to a complex consisting of effusive rocks of intermediate and basic composition which is Lower Devonian in age, and found at the present time in the Lower Devonian deposits of the Turkestan-Alsisk zone [23].

From the brief description of the material composition of the mineral associations, it is evident that the petrographic composition of the eroded areas did not remain constant, but rather varied both in space and in time. A change in the petrographic composition can be identified in the Jurassic deposits of Southern Ferghana by the formation of mineral associations characterized by different material compositions. Each such change corresponds to a definite stage in the tectonic development of the region and reflects specifics associated with the petrographic background of the region of drift.

The Eastern Border of the Basin. For a characterization of the sections of Eastern Ferghana, we used the material of O. G. Larina et al. [20] along with our own data. The sections of the Kok-Yangaksk coal deposit were the object of study. Three mineral associations can be delineated within the composition of the Jurassic deposits in this region: and oligomictic-quartzitic association, an oligomictic-quartzitic association with a high content of fragments (characteristic of the deposits of the first and second macrocycles) and a feldspathic-quartzitic association (established within composition of the third macrocycle). The first two associations differ from one another in composition only with respect to quantitative content of rock fragments (from 20-30% in the first association and from 30-40% in the second). In addition, 10 to 15% feldspar is present in the second association.

A transparent, fissured type of quartz free of inclusions is the most abundant type. Quartz with elongated grains extended along the c axis is present in small quantities. It is also transparent and devoid of inclusions. Quartz which is isometric shape and which shows inclusion of zircon, tourmaline, and apatite is found in the form of individual grains. Rock fragments are represented by siliceous-sericitic shales quartzites, and jaspers. The jasper fragments consist of pelitomorphic crystalline silica, sometimes with the remains of radiolarians. Of the micaceous minerals, we find biotite, chlorite, and, in small quantities, muscovite is present. The clay minerals are represented by hydromica and kaolinite.

The composition of the third feldspar-quartz association differs somewhat from the compositions of the first two associations. This difference includes a decrease (up to 40-50%) in the quartz content and an increase (up to 20%) in the feldspar content. The concentration of rock fragments does not exceed 35%. In contrast to the preceding associations, there is a significant increase in grains of "striated" quartz with inclusions of zircon and apatite. Jaspers and quartzites are common among the rock fragments. In addition, fragments of microgranites and effusive-rock occur in this association. From among the accessory minerals, one finds ilmenite, leucoxene, zircon, garnets, tourmaline, epidote, and titanium-bearing minerals. Chlorite, montmorillonite, and mixed-layer formations of hydromicaceous-montmorillonitic composition occur along with kaolinite and hydromica.

The analysis of the composition of the mineral associations provides a basis for suggesting that various sources rocks were involved during the formation of the associations. In particular, as was noted above, quartz and fragments of various rocks take on a primary role in the composition of the first two associations. The composition of the accessory minerals is very specific, zircon, tourmaline, rutile, garnet are among the most stable of the clay minerals. Note the absence of femic minerals, i.e., hornblende, pyroxenes, and other minerals widely distributed among the Paleozoic rocks, in the compositions of the associations. They all belong to a group of unstable components found in so-called stable minerals.

A. G. Kossovskaya [17] believes that their absence is connected with type-alteration processes affecting the original fragmental material as a result of natural selection, i.e., a destruction of the unstable mineral component and an accumulation of stable ones. Such a process could have proceeded under two different conditions: during the stage of weathering of the Paleozoic rocks and during catagenesis [17].

In our particular case, destruction of the unstable mineral components took place during the stage of the weathering of the pre-Jurassic formations. Processes of catagenesis are weakly expressed here. Phyllites, siliceous, quartzic-micaceous, and other shales broken by granites should be classified as the primary sources. A similar complex occurs among rocks of Middle Paleozoic age [10]. In this case, the most weathered horizons underwent erosion during the formation of the first association and horizons of less weathered rock were involved at the beginning of the deposition of the second association in the region of denudation.

The third association can be distinguished from the first two by the occurrence of feldspars and by the more varied selection of accessory and clay minerals in its composition. A similar change in the material composition of the mineral association could be caused by a change in the petrographic composition of the eroded areas. Together with the complex described above (the role of which was abruptly curtailed), the intrusive complexes began to undergo erosion. At the present time, they have a limited distribution. It should be noted that they were widely distributed in the region of denudation at the time when the third association was formed.

The Northeastern Border of the Basin. In contrast to other regions, an abrupt increase in arkosic content took place in the Jurassic deposits of Northeastern Ferghana due to the involvement of strictly magmatic rocks in the region of sediment accumulation; this is confirmed by the composition of the mineral associations.

A feldspar-quartz association is characteristic of the sediments of the first and second macrocycles of the Tashkumyr section. It has the following composition: 70-75% quartz; 20-25% feldspars; up to 10% rock fragments. The feldspar are represented by plagioclase and potassic varieties.

Grains of the feldspars are, in a number of cases, entirely replaced by calcite. In such cases, the quantity of rock fragments is sharply increased in the rock, so that an incorrect interpretation could lead to erroneous conclusions concerning the questions of origin.

Quartz is represented by an isometric-tabular variety, frequently with inclusions of accessory minerals. The rock fragments consist of siliceous and clayey shales. Among the accessory minerals, one can find zircon, tourmaline, garnet, sphene, epidote, and magnetite. In addition, kyanite, zeisite, and leucoxene have been described in this portion of the section [3]. The clay minerals consist of hydromica and kaolinite.

An arkosic association was established in the alluvial deposits of the third macrocycle of the section at Tashkumyr. Concentration of quartz ranging from 40-50% and concentrations of feldspar ranging from 40-60% are characteristic of this association. The quantity of rock fragments does not exceed 5%. In general, this association differs from the one described above with respect to material composition only in having high content of feldspars and a decreased quantity of rock fragments. Hydromica, chlorite, and montmorillonite are among the clay minerals encountered. Kaolinite is present in the form of an admixture.

From this short characterization of the material composition of the mineral associations, it is evident that they differ from all associations described above in having high concentrations of feldspars (especially in the third macrocycle), with orthoclase being the most abundant. Plagioclase occurs in smaller quantities and can be classified as oligoclase. Quartz is primarily represented by an "eruptive" type characterized by an absence of traces of rounding. The composition of the accessory minerals is characteristic; it includes zircon, leucoxene, tourmaline, magnetite, and others.

Thus, the associations are most reminiscent of granitoid rocks with respect to material composition. Apparently, the granitoid massif located within paleo-Kuramino-Chatkal resembles the associations described above [15]. Material from sedimentary-metamorphic complexes arrived into the region of sedimentation in parallel with the erosion of the intrusive rocks at this time.

Further along in the formation of the third association, the intensity of the erosion of the intrusive complexes increased sharply. The role of the metamorphic rocks became minor, and, in a number of cases, disappeared completely.

The Northern Border of the Basin. The Jurassic deposits have been studied most completely along the Arkit section (Fig. 1). In addition to our own data, we have used the materials of V. A. Babadagl and A. Dzhumangulov [3] in analyzing this area. Two associations can be delineated in the deposits of Jurassic age: a quartz-graywacke association and a felspar-graywacke association with a high content of effusive-rock fragments. The first association is the most clearly represented in the alluvial and lacustrine sediments of the Lower and Middle Jurassic (the first and second macrocycles). Its formation proceeded under humid climatic conditions. The second association was established in the alluvial deposits of the Upper Jurassic (the third macrocycle). It was formed during an aridization of the climate. The material composition of the mineral associations of Northern Ferghana differs from the preceding mineral associations. This difference is due to somewhat elevated concentrations of feldspars (up to 30%) and rock fragments (up to 20%) in the midst of an overall decrease in the concentration of quartz (the association consists of not more than 60% quartz). The feldspars are represented by very different varieties: orthoclase, microcline, and albite. Sericitized and pelitomorphic grains, both relatively fresh, are present among them. The most abundant of the rock fragments are siliceous-sericitic shales and quartzites. Fragments of effusives of andesitic composition, and also fragments of acidic and ultrabasic rocks represented by microgranites and micropegmatites are present in small quantities. The accessory minerals are especially varied. The magnetite-ilmenite-leucoxene association enjoys the greatest abundance among the ore minerals. Garnet, sphene, kyanite, and staurolite are among the stable minerals encountered. Only epidote and zoisite need be mentioned from among the moderately stable minerals. Zircon and tourmaline are among the extremely stable minerals. Among the clay minerals, one finds hydromica, kaolinite, and chlorite. Similar material compositions are characteristic of the deposits of the first and second macrocycles.

The compositions of the associations change along the section. These changes are connected with the abrupt increase in fragments of effusive rocks with acidic and basic compositions. There is somewhat of a decrease in the content of feldspars in this association, which is interesting. The accessory minerals are identical to those in the association described previously. The difference consists in the sharp decrease in the content of magnetite and ilmenite.

The composition of clay minerals is extremely varied. Kaolinite, hydromica, chlorite, vermiculite, mixed-layer formations of a hydromicaceous-montmorillonitic composition, and mountain leather (?) are among these. This association can be reliably delineated within the deposits of the third macrocycle.

The material presented indicates that Paleozoic formations of diverse petrographic compositions were subjected to erosion in the midst of the source rocks. In particular, sedimentary-metamorphic and intrusive complexes not subjected to significant weathering processes were eroded during the formation of the first association. These are the Paleozoic granitoid massifs and sedimentary-metamorphic complexes of paleo-Chatkal-Kuramin. The compositions of the light and heavy fractions do not contradict this assertion [14, 15].

During the formation of the second association, substantial changes occurred caused by the appearance of diverse intrusive complexes of acidic and basic composition in the sources of the drift. Judging from the composition of the rock fragments, they correlate with spilites, porphyrites, dacites, and other effusive complexes which occur at present within the modern mountain ranges.

The Eastern Ferghana Basin

This sedimentary basin is characterized by a specific complex of clastogenic material. The diversity with regard to sources of drift is reflected in even in such a limited territory as the Eastern Ferghana basin. Two regions differing sharply in material composition can be delineated within its borders.

In sections overhanging the Talas-Ferghana fault, siliclastic-quartzitic and quartz-graywacke (second macrocycle) associations were formed. They are very similar in material composition their difference consists in an increase in rock fragments from 5-15% (in the composition of the first macrocycle) up to 30-40% (in the second) and an almost complete absence of feldspars (Figs. 1, 2).

The sedimentational-sedimentary type of quartz is the most abundant. Effusive quartz is present in small quantities. The rock fragments are quite varied. Silty-clayey, clayey, and siliceous shales in an intermediate stage of metamorphism can be found here. Microlayering can be clearly seen in the fragments of the clayey shales. Grains of quartz are present in the groundmass. Fragments of acidic effusive rocks are present in small quantities.

The micas are represented by biotite and muscovite. Among the accessory minerals one finds stable varieties such as zircon, tourmaline, and staurolite, among the clay varieties, hydromica and kaolinite are present.

A somewhat different composition of Jurassic deposits exists along the eastern slope of the Yaassinsk water-divide. The difference in material composition is expressed in an increase in the polymictic character of the deposits. In the deposits of the first macrocycle along the Beshterek, Karashur, and Karashura-1 sections, in particular, a mesomictic-quartzitic association was established which has the following composition: 50-60% quartz; 20-30% feldspars; 15-20% rock fragments (see Figs. 1, 2). Grains of irregular-isometric shape with fine needle-like inclusions of rutile occur among the quartz. A type second in importance is clear; the grains are found with sparse, usually linearly oriented, minute gas-liquid inclusions.

Reworked sedimentary quartz is present in small quantities. Plagioclase and the potassic varieties are among the types of feldspars encountered. As a rule, a significant portion of the feldspars are completely replaced clayey material or calcite. In the first case, their alteration is connected with the source of drift; in the second case, it is connected with changes in the Jurassic sedimentary basins themselves, changes which took place during catagenesis.

The plagioclases are impoverished in composition and are characterized by the presence of primarily acidic varieties (below No. 20). This is due both to the composition of the source rocks and the processes of post-sedimentational alteration. Acidic and basic effusives, siliceous shales, and quartzites are among the rock fragments present. Large quantities of hydrated biotite can be found in the association. The accessory minerals are represented by zircon, tourmaline, rutile, magnetite, ilmenite, staurolite, sphene, and apatite.

Along the section, the mesomictic association changes into a graywacke-arkosic association. This transition is due to a decrease (up to 40-60%) in quartz and an abrupt increase (up to 50%) in feldspars. The concentration of rock fragments remains the same, not exceeding 15%. Microcline, together with plagioclase and potassic varieties, are among the feldspars found. The specific composition of the rock fragments, among which effusive and magmatic varieties can be found, also changes in this association. The accessory minerals are represented by the same varieties found in the first association. Hydromica and kaolinite are among the clay minerals present.

On the basis of the data given above, one can clearly define a sharp difference in the material compositions of the mineral associations, despite the fact that the associations occur at relatively small (no more than 50-60 km) distance from one another. These differences are primarily due to the character of the source rock.

In particular, during the formation of the siliceous-quartzitic and quartz-graywacke associations in the sections established at Kok-Kiya and Tuyuk, it was primarily various sedimentary and metamorphic rocks, as confirmed by different degrees of weathering, which underwent erosion. In this case, judging from the character of the fragmental portion of the minerals, the light and heavy fractions and the source rocks were located at various distances from the Jurassic sedimentary basins. If the drainage areas were located in direct proximity to the sedimentary basins in such a case, the terrigenous minerals, as a rule, would be characterized by slight rounding or a total absence of rounding. On the other hand, if the sources of drift were located at a significant distance from the zone of accumulation, the terrigenous minerals would take on clearly expressed rounded and semirounded shapes; this would be insured by the long migration paths of the terrigenous material. The points mentioned above are in agreement with data on the paleogeographic reconstruction of the Jurassic sedimentary basins.

We suggest that the siliclastic-quartzitic and quartz-graywacke associations were formed from at least two sources of drift. One of these was located near the sedimentary basin. It was most likely the sedimentary-metamorphic Middle- and Upper-Paleozoic complex of the

Yassinsk water-divide. The material composition of these complexes, as our investigations have shown, were inherited to a significant degree by the Kok-Kiya and Tuyuk sections. The weathered complexes of the pre-Jurassic formations located east of the Telas-Ferghana fault and within the paleo-Narynsk land were a second source of drift. This region was a region of denudation where weathered crusts were widely distributed, not only over the course of the Jurassic, but also during Cretaceous times.

The third and fourth associations, as noted above, differ sharply from the first two associations in material composition. This difference consists in the occurrence of magmatic and effusive rocks along with the sedimentary and metamorphic rocks (the roles of which are sharply reduced) in the sources of drift. Judging from the material composition of the mineral associations, these may have been acidic and basic effusives in one case, and, in addition, a complex of granitoid rocks in the other. At the present time analogous complexes are not found in the compositions of nearby rises. It is not excluded that they may have existed in the region of the Yassinsk anticline in the past. It is difficult to assume that granitoid and effusive massifs located at significant distances from the Jurassic basins served as the source of drift for these associations. Taking into consideration the long path of transportation, a more or less good degree of sorting and rounding of the minerals in both the light and heavy fractions would be anticipated, if that were the case. This was not confirmed in our investigations, however. Apparently, an answer to these questions will require further, more detailed investigations.

The data presented on the material compositions of the Jurassic deposits indicates that the formation of the deposits took place under various tectonic regimes, climatic conditions, and the erosion of rock complexes with especially varied petrographic compositions. As is evident from the triangular diagram (Fig. 2), a general pattern expressed by an increase in the polymictic character of the Jurassic deposits upwards along the section occurs in almost all of the sections; this is reflected in the increased contrast between tectonic movements. The latter correspond on the triangular diagram to a shift of figurative points for the composition of sandy-gravelly rock from the upper monomictic portion of the triangle to the lower polymictic half of the triangle, i.e., toward the base [26]. This tendency is a reflection of geological events which correspond to the pre-Jurassic and Jurassic stages of sediment deposition. After the end of Hercynian folding, the territory in southeastern Central Asia, including the territory we studied and the adjacent regions, entered a new stage in its evolution: the levelling of the Hercynian mountain ranges. The presence of weathered crust under the Jurassic deposits in the area is an indication of the intensity of chemical and physical weathering processes accompanied, in a number of cases, by the formation of bauxites within the borders of this vast region [5, 8, 9, 12, 19]. In the opinion of these investigators, the age of the weathered crust can be established as Middle-Upper Triassic.

A new stage in the evolution of Central Asia began in early Jurassic times. It was expressed by an abrupt activation of tectonic processes and by the initial creation of the river valley and individual sedimentary basins. The primary suppliers of terrigenous material to these sedimentary basins were pre-Jurassic weathered crusts; this is indicated by the material compositions of the deposits of the first and second macrocycles, represented by mainly by quartz in concentrations reaching 90%, by the stable associations of clay minerals with kaolinite and hydromica dominating and tourmaline, and by zircon, and rutile dominating among the accessory minerals. All of this unequivocally confirms an erosion of weathered crusts. With respect to size, there is a general tendency for a change in material composition toward an increased polymictic character; this is expressed in a change of terrigenous-mineral associations, indicating that less weathered, and, in a number of cases, fresh rocks were successively involved in the region of sediment deposition. The change in terrigenous-mineral associations in time and space is not incidental, but rather reflects fundamental stages in tectonic activity not only with the regions studied but also in adjacent territories. The investigations of P. P. Timofeev et al [27], B. C. Plyanskii [22], and V. I. Troitskii [29] indicate that the stages of tectonic activity had a regional character and were expressed by a change in the environment of sedimentation and peat accumulation, group composition of plant associations [1, 11, 13] and climate.

The first stage covered the Lower Jurassic and Aalenian; it was characterized filling of the first river valleys and individual sedimentary basins. The second stage corresponds to the Bajocian-Bathonian times and reflects a stage of relative attenuation of tectonic processes. This stage coincides with the maximum development of landscapes with large-scale

fresh-water lakes. In particular, the territory of Central Asia at the end of the third stage turned into a region of denudation. Moreover, a change in climate from arid to humid is connected with this stage. Within the composition of these large-scale mineral associations, one can undoubtedly delineate smaller mineral complexes with distributions in the section and over the area reflecting different details in the history of terrigenous sediment deposition with the territory being described. The problem of establishing the chief mineral associations and their correlations with the overall course of sediment accumulation became part of our task.

In conclusion, it is desirable to note that any investigations, including stratigraphic investigations, are incomplete without thorough studies of the material compositions of the formations, studies which give a clear understanding of the evolution of the ancient distributive provinces, the tectonic regime, and the landscapes of the sedimentary basins in past geological epochs.

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POLYMETALLIC MINERALIZATION IN METASEDIMENTARY
FORMATIONS OF THE UKRAINE (GENETIC TYPES, FORMATION
CONDITIONS, AND MINERAL TYPOMORPHISM)

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UDC 553.45'319'(477)

The role of post-sedimentary alterations of sedimentary rocks in the formation of polymetallic mineralization is discussed in this article. On the basis of the stages of alteration, sedimentary-diagenetic, catagenic, and metagenetic types of ore concentrations are distinguished that are defined by the thermodynamic conditions of formation and typomorphic characteristics of the ore and gangue minerals.

In recent years formations of what are known as telethermal and stratiform deposits have been explained in terms of post-sedimentary developments of sedimentary formations [11, 18, 19]. According to these hypotheses, the vast majority of ore concentrations in metasediments formed as a result of the primary accumulation of substance during the stage of sedimentation and the subsequent redistribution of this material as a result of the processes of lithogenesis with the active involvement of fluids.

The degree of redistribution of the primary sedimentary ore-forming elements is directly dependent on the post-sedimentary alteration of the sedimentary sequences. The composition, the conditions under which the deposits formed, and the typomorphic properties of the minerals are determined by the thermodynamic parameters of the stages of the transformation and by the chemical and mineralogical characteristics of the sediments.

In connection with the above we have studied the polymetallic mineralization of the Ukraine localized in sedimentary formations that have experienced different stages of transformation in the evolutionary sequences: diagenesis-catagenesis-metagenesis [10, 14]. The most favorable region for this type of study is the Donbass, where metamorphic vein-type and disseminated mineralization is widely distributed throughout the rocks of terrigenous coal-bearing formations. In the axial part of the basin are concentrated well-known polymetallic deposits and ore shows, the origin of which is the object of a certain amount of dispute. A characteristic feature of the region is the fact that the rocks have undergone the entire gamut of post-sedimentary transformations, beginning with diagenesis and ending with late metagenesis, which made it possible to trace the change in the conditions of formation and the typomorphic characteristics of the minerals as a function of the degree of transformation of the host rocks. Information on the Donbass is logically related to and complemented by the sulfide showings of the Dnieper-Donets Basin (DDB), the Pridnestrov'e, and the Pri-karpat'e.

The thermodynamic boundaries of the stages of lithogenesis are defined on the basis of the degree of coalification of the organic matter as determined by the methods of thermobaric geochemistry and mineralogical-geochemical studies. The stage of catagenesis is defined by the first appearance of calcite veins in the rocks, and the stage of metagenesis by the appearance of quartz veins. The boundary between catagenesis and metagenesis is found in the transition zone between lean-coking coals and lean coals.

Depending on the history of the sedimentary formations, the ore accumulations localized in them can be divided into sedimentary-diagenetic, catagenic, and metagenic types in accordance with the stages of the alteration referred to above.

Institute of the Geochemistry and Mineral Physics, Academy of Sciences of the Ukrainian SSR, Kiev. Translated from *Litologiya i Poleznye Iskopaemye*, No. 5, pp. 58-69, September-October, 1987. Original article submitted June 3, 1986.

The problems associated with diagenesis and diagenetic ore formation have been treated in some detail by N. M. Strakhov [15]. A major and controlling factor of diagenetic processes is the decomposition of the organic matter responsible for a producing the reducing environment. Paralleling the decomposition of the organic matter, the Pb, Zn, Cu, Fe, and other elements present in the sediment as oxides and carbonates are released to the solution. The ore-forming elements react with the sulfuric acid produced by the reduction of sulfate to give low-solubility sulfides in the form of colloidal solutions. The resulting nonuniform distribution of pH and Eh inevitably leads to the agglomeration of the colloidal particles into separate regions, and hence the accumulation of sulfides in the form of disseminations, nodules, and concretions. The best evidence of this type of process is provided by the phosphorite and carbonate-clay sulfide-bearing concretions of the Pridnestrov'e and the Donbass, and also the nodules in the coaliferous sequence.

The overall geological position and mineralogy of these formations has been studied in detail by E. K. Lazarenko, B. I. Srebrodol'skii [13], and P. V. Zaritskii [8]. We merely note that the diagenetic origin of the concretions is not doubted by anyone, but the ore mineralization localized in them is considered to be late. We shall present new data in favor of the sulfide minerals forming syngenetically with concretion-formation.

We have made the first electron-microscopic study of the internal structure of the individual mineral grains and aggregates of sphalerite, halite, chalcopryite, and pyrite from the formations referred to. The sulfides are found in the centers of the phosphorite and carbonate-clay concretions, often filling the cavities and syneresis cracks. The individual sulfide grains form elongated segregations along the radial fibers of the phosphate and clay-carbonate material. Study of the mineralogy showed that the sulfides are characterized by a homogeneous internal structure and hypidiomorphic overgrowths. Electron-microscope studies detected a uniform internal structure of the minerals, which provides a background against which can be seen relicts of the collomorphic formations and gels with a composition corresponding to that of the host mineral, which was identified by their microfracture pictures.

Sphalerite. In the sphalerites, dendritic (Fig. 1)* and globular segregations (Fig. 2) are often detected, evidence of crystallization of the zinc sulfide from strongly supersaturated (colloidal) solutions. The formation of these segregations can be explained as being

*The photomicrographs were made on EBM-100L electron microscope by the self-shading carbon replica method from freshly cleaved minerals. The analyst was V. V. Burmistrova.

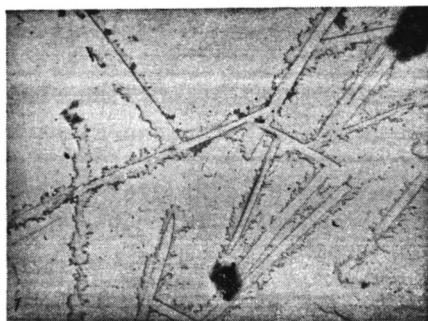


Fig. 1



Fig. 2

Fig. 1. Sphalerite from a clay-carbonate concretion of the Donbass. Dendritic segregations of ZnS along microcracks in ground mass of sphalerite. $\times 12,500$.

Fig. 2. Sphalerite from a phosphorite concretion of Pridnestrov'e. Globular and droplike segregations of residual ZnS on the surface along microcracks of sphalerite. $\times 15,000$.

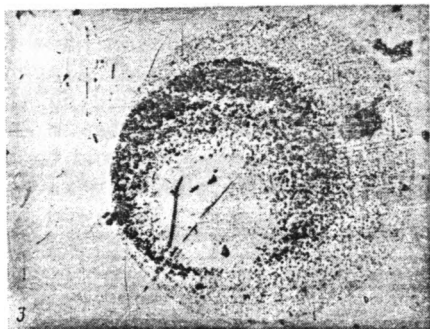


Fig. 3

Fig. 3. Galena from a phosphorite concretion of Pridnestrov'e. Drop of residual PbS gel on one of the faces of earlier formed galena crystal. $\times 7800$.

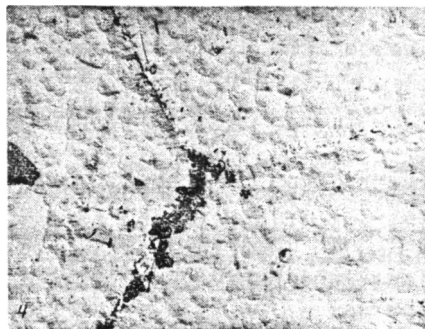


Fig. 4

Fig. 4. Pyrite from carbonaceous formation of the Donbass. Partially crystallized nodular formations of pyrite with syneresis microcracks filled with calcite. $\times 9500$.



Fig. 5

Fig. 5. Chalcopyrite from a phosphorite concretion of Pridnestrov'e. Transition of globular formations to crystalline aggregates with relicts of drops of residual CuFeS_2 gel. $\times 11,100$.

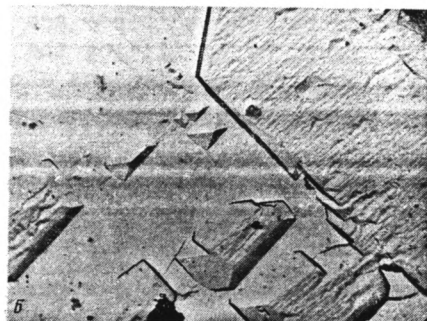


Fig. 6

Fig. 6. Pyrite from a calcite vein. Dronovsk anticlinal, Donbass. Idiomorphic segregations of bismuth in pyrite. $\times 9400$.

due to the preservation of the relicts of the coagulate in regions where the individual grains grew undisturbed, possibly in dislocation zones. Furthermore, on the surfaces of the sphalerite crystal faces large segregations of tiny spherules of ZnS are observed uniformly distributed over the entire mass, the dimensions of the spherules varying over wide limits. The formation of such microstructures is explained by the precipitation of charged coagulates at electrodes, here the forces of previously formed crystals.

Galena. While colloform structures are encountered rather frequently in sphalerite, detecting relicts of PbS gels is a rare occurrence in mineralogical practice, is of special interest, since due to its ease of crystallization galena is virtually unknown in typical collomorphic aggregates. The structure depicted in Fig. 3 formed by the coagulation of a colloidal solution and its precipitation on previously formed galena crystals. The spherical cloudlike shape indicates that the colloidal solution was an emulsionlike liquid with suspended drops of the PbS coagulate.

Pyrite and Chalcopyrite. Relicts of globular structures have also been found in crystallized pyrite and chalcopyrite. As these minerals crystallize, the coagulates that have settled out age and undergo a number of alterations. This is primarily expressed in the further growth of the crystalline particles, and their segregation into the large crystals. This relationship between the colloidal and the crystalline formations is illustrated in Figs. 4 and 5, where the transformation of collomorphic pyrite and chalcopyrite into distinctly crystalline aggregates of the same chemical composition is clearly visible. As crystallization

proceeds it is accompanied by the gradual dehydration of the coagulates, which is reflected in the appearance of syneresis cracks (Fig. 4). The partially crystallized nodular pyrite formations are cut by radial dessication microcracks filled with calcite.

Limiting ourselves to the examples given above, the absence in them of microinclusions of other minerals should be especially emphasized. This is evidence that the crystallization of the sulfides occurred within a single physicochemical system strictly according to the sequence of formation governed by the coagulation threshold of the colloidal solutions, the optimal conditions for the formation of which arise during the reduction stage of diagenesis [15]. Coagulation of the colloids and the formation of are accumulations occurred at successive stages of diagenesis.

The high concentration of the solutions is also suggested by the results of a study of inclusions of the mineral-forming medium in the sphalerite and calcite from the phosphorite and carbonate-clay concretions. In these minerals only the presence of single-phase liquid inclusions was detected, unambiguous evidence of cold solutions. The concentration of the salts as determined by cryometry is 15-20% NaCl equivalent. In the gas fraction of the inclusions compounds such as CO and CH₄ predominate, indicating a reducing environment of mineralization.

That microbiological processes played an important role in the formation of the diagenetic sedimentary sulfides is indicated by the results of a sulfur isotope study ($\delta^{34}\text{S} = +4.6$ to 17.6‰). Such enrichment in the heavy isotope is characteristic of sulfur formed by the reduction of the sulfate sulfur of sedimentary waters by organic matter.

On the whole, all the sulfides of diagenetic sedimentary origin have been shown by this study to exhibit a number of characteristic features of colloidal formations: nodular and dendritic aggregates, a cryptocrystalline structure, the presence of spherules consisting of the relicts of gels of the corresponding composition, the absence of microinclusions of different minerals, and a high concentration of mineral-forming solutions in inclusions. Based on this evidence it is established that in the formation of the diagenetic sedimentary ore accumulations the major role was played by colloidal solutions.

GENETIC FEATURES OF CATAGENETIC SULFIDE FORMATION

Catagenic changes in rocks are caused by pressures up to 1000 atm, temperatures up to 180°C, and increases in the activity and importance of the role of fluids. The major phase of petroleum formation occurs under the thermodynamic conditions corresponding to catagenesis [2], accounting for the identity of sources, and the spatial and genetic links of the catagenic ore concentrations and the hydrocarbon deposits.

On the one hand, catagenic processes are in a way a continuation of the diagenetic processes, and on the other hand, they gradually pass into metamorphic processes. Catagenic mineralization differs from the diagenetic formation of ore concentrations in the recrystallization and redeposition of the sulfides. During catagenesis, lithification and compaction of the rocks occur, with the migration of sedimentary and pore fluids from fine-clastic to coarse-clastic types, thereby contributing to the cementation of the latter by carbonates, sulfates, and sulfides. The alteration of the clastic components occurs as a result of dissolution under pressure and metasomatic replacement in the presence of pore and interstitial solutions [14].

Redeposition, cementation, and metasomatism occur under significantly different physicochemical parameters, which is responsible for the difference in the mineral composition of the ores and the typomorphical features of the minerals. Evidence of this is provided by studies of sulfide minerals and associated minerals from a number of deposits and ore showings of the Donbass, the Dnieper-Donets Basin, and the Prikarpat'e which formed at the catagenetic stage of the transformation of the sediments and which are characterized by the same genetic features (Table 1).

The variegated and compositionally varied paragenetic mineral assemblages of the catagenic ores (sphalerite + galena + pyrite + marcasite + barite + calcite + anhydrite + sulfur + hydrocarbons) are generally encountered in the form of cements and metasomatic dissemination in the country rocks, more rarely in the form of veins. Quartz is lacking in the ore parageneses.

A characteristic feature of the internal structure of the sulfides studied is the presence of typical colloform microstructures and obviously crystalline structures with large quantities of microinclusions of different minerals (Fig. 6), evidence that they formed from both colloidal and true solutions. The geochemical specificity of the ore minerals is fairly constant for all the deposits studied. The sphalerite is characterized by a low iron content and an elevated cadmium content. The galena lacks virtually any of the trace silver, bismuth, and antimony characteristic of this mineral.

In considering the isotopic composition of the sulfur (Table 1) the rather substantial scatter in the $\delta^{34}\text{S}$ values reflecting the complexity and specificity of the formation conditions must be noted. The most instructive example in this regard is the polymetallic mineralization in the carbonaceous deposits of the Bakhmut basin and the Truskavetsk lead-zinc deposit in the Prikarpat'e, the formation of which involved chloride-sodium-calcium metalliferous brines and infiltrated sulfate-rich waters [4, 12]. Only the direct contact of different hydrochemical media could form the sharp oxidation-reduction barrier that contributed to ore deposition and the formation of the variegated mineralic composition of the ores.

In order to indicate the characteristic features of catagenic mineralization we shall give a brief description of the data for the Truskavetsk sulfur-polymetallic deposit. Almost all ore concentrations that can be classified as catagenic can be compared to at least some degree with this deposit.

The deposit includes sandy-argillaceous carbonate beds of the Lower Vorotyshensk Miocene, which form an anticlinal structure. The overlying strata are a saliferous Upper Vorotyshensk suite. The major ore minerals are represented by a cryptocrystalline zinc sulfide (brunkite) and galena. Pyrite, chalcopyrite, and marcasite are encountered in small amounts. Of the gangue minerals, native sulfur, gypsum, anhydrite, barite, and calcite should be noted.

In this region there is oil, ozocerite, and other hydrocarbon compounds, and therefore the formation of the lead-zinc ores can most likely be considered to be closely related to that of the hydrocarbons. As a result of catagenesis, a fairly significant amount of aqueous solution is removed from the pelitic argillaceous sediments which subsequently forms aqueous layers. In the oil and gas bearing regions, the underground stratified waters are chloride alkali-earth/sodium brines and are usually the contour waters of petroleum deposits [5]. As the sediments were transformed, the adsorbed ions of the ore elements were also liberated to the aqueous solutions. In addition, the thermal brines leached the heavy metals and ores of other components from host rocks previously enriched in lead, zinc, copper, and other metals. Thus, at the onset of ore formation the thermal solutions described were enriched in components encountered in the mineral assemblages of the Truskavets deposit and where in modern times the presence of hot metalliferous brines with mineralization up to 400 g/liter have been detected.

In the zone of the deposit, geochemical barriers of two kinds formed, a hydrogen sulfide barrier and a sulfate barrier. Their formation was due to the concentration of hydrogen sulfide gas in the apical part of the anticlinal and the presence of halide rocks of gypsum-anhydrite composition. The formation of the deposit begins at the moment when the metalliferous brines have penetrated to the discharge area, the arch of the anticlinal structure. Here the brines are enriched in hydrogen sulfide, which is what caused the precipitation of the dissolved metals in the form of gels.

In the region of the circulation of infiltration sulfate waters, barite, celestite, anhydrite, and other associated minerals precipitated out of the brines. Native sulfur precipitated out along with the ore and gangue components. Its formation is confined to two stages, one of reduction and one of oxidation. In the first stage the sulfur formed by the reduction of the sulfate ion according to the equation $\text{SO}_4^{2-} + 2\text{H}^+ = \text{S}_8 + \frac{3}{2}\text{O}_2 + \text{H}_2\text{O}$ simultaneously with sulfide formation before the geological structure was completely exposed. The second generation of sulfur formed by the oxidation of hydrogen sulfide as the structure was being exposed, i.e., when there was unhindered access of oxygen, according to the equation $\text{H}_2\text{S} + \frac{1}{2}\text{O}_2 = \text{S}_8 + \text{H}_2\text{O}$.

The formation of the mineral assemblages of the Truskavetsk deposit described above is confirmed by isotopic and geochemical investigations (Table 1). The narrow limits of the isotope ratios and the enrichment of the sulfide sulfur in the light isotopes is evidence

TABLE 1. Some Genetic Characteristics of Ore Minerals Formed during the Catagenic Stage of Alteration of the Sedimentary Rocks of the Ukraine

Deposit or ore show	Mineral assemblage	Mineral	Temp. of formation, °C	Contaminant elements	$\delta^{34}\text{S}$, ‰
Eastern bank of the Bakhmutsk basin	Sphalerite + galena + pyrite + marcasite + chalcopyrite + barite + calcite	Sphalerite	145—173	Cd, Hg, Tl	-135,3
		Pyrite	140—200	Tl, Pb, Co	+16,8÷+32,2
		Galena	60—100	Tl, Pb, Co	-27,7÷-34,1
			115—130	—	-5,6
Truskavetsk	Sphalerite (brunkite) + galena + pyrite + chalcopyrite + gypsum + barite + native sulfur + ozocerite	Brunkite	45—110	Cd, Mn, Tl, Ga	-0,1÷-0,4
		Galena	45—75	Tl	-10,3÷-3,8
		Pyrite	100—110	Cu, Tl, Co	-13,5
		Sulfur	—	—	-15,1÷-14,5
		Gypsum	—	—	-4,3÷-34,2
		H ₂ S source	—	—	-15,7÷-134,2
		SO ₄ source	—	—	-14,1÷-31,7
Donets	Sphalerite + galena + pyrite + marcasite + calcite + barite	Sphalerite	100—125	Cd, Ga, Ge	-7,3
		Pyrite	—	—	-116,5
Pervomaisk (Donbass)	Pyrite + marcasite + chalcopyrite + calcite + barite	»	110—135	Co, Tl, In	-14,0
Yablunovsk (DDB)	Sphalerite + pyrite + barite + calcite	Sphalerite	150—175	Cd, Ge, Tl	-15,0

Note. The temperatures of formation of the minerals were determined by homogenization and decrepitation of fluid inclusions and on the basis of thermoenergy dispersive spectroscopy of pyrite and galena. The isotopic analysis of sulfur was performed at the Department of Stable Isotope Geochemistry of the Division of Metallogeny of the IGFM of the Academy of Sciences of the Ukrainian SSR. The analyst was V. I. Vlasenko. The information on the isotopic composition of sulfur of the gangue compounds from the Truskavetsk deposit are from [3].

of the participation of the hydrogen sulfide of the petroleum deposits in the formation of the ore. The wide limits of variation of the $\delta^{34}\text{S}$ of the elemental sulfur are due to its formation at different stages and by different processes. The native sulfur formed by sulfate reduction is enriched in the heavy isotope ($\delta^{34}\text{S} = +5.1$ to $+14.5\text{‰}$), and the sulfur formed by oxidation of hydrogen sulfide is enriched in the light isotope ($\delta^{34}\text{S} = -4.3$ to -34.2‰).

The isotopic composition of the calcite carbon found in association with native sulfur, brunkite, and galena, has ^{13}C values between -20 and -30‰ , which corresponds to the isotope composition of the carbon of petroleum. It is likely that carbonic acid was involved in the formation of the calcite, the gas being evolved by reaction of the sulfate with the organic compounds according to the equation $\text{CH}_4 + \text{SO}_4^{2-} + 2\text{H}^+ = 2\text{H}_2\text{S} + \text{CO}_2 + 2\text{H}_2\text{O}$.

A similar mechanism for the formation of catagenic sulfide concentrations and their relationship to gas and oil deposits have been established for many regions in the USSR and abroad, which allows us to speak of the regional nature of the processes described above.

The data presented above allow us to outline the following typomorphic features of catagenic sulfide minerals: a varied and variegated mineral compositions and the presence in the ores of barite, marcasite, and hydrocarbons; the development in the ore minerals of both typical collomorphic internal microstructures as well as clearly crystalline heterogenic structures with large quantities of microinclusions of other minerals; the presence of elevated concentrations of Cd, Tl, Ga and the lack of traces of Ag, Sb, and As; the varied isotopic composition of the sulfur of the sulfides and the associated minerals with broad dispersions both in the direction of light as well as heavy isotopes; the spatial and genetic links of the ore concentrations with hydrocarbon deposits.

CHARACTERISTICS OF METAGENETIC MINERAL FORMATION

Metagenesis involves the extensive structure and mineralogical alteration of sedimentary rocks in the lower part of the stratisphere and is similar in nature to the initial stages of regional metamorphism [14]. The stage of metagenesis is characterized by temperature of $180\text{--}400^\circ\text{C}$ and pressures of $1000\text{--}2500$ atm. Metagenetic alterations of ore-bearing sedimentary rocks are normally accompanied by the intensive migration of ore and gangue components, their segregation and selective recrystallization. As a result of these processes, vein and veinlike bodies form, as well as large individual metacrystals of sulfide minerals.

In the Ukraine, the clearest example of a metagenetic formation is the polymetallic mineralization of the Nagol' Ridge in the central part of the Donbass, part of the brachianticlinical structures of the Main Anticlinal. For the deposits and ore shows, vein and stringer types of mineralization, as well as accumulations of metacrystals of pyrite and arsenopyrite in sand-clay rocks, are characteristic. The mineral composition of the veins is complex and varied. The major ore minerals are sphalerite, galena, pyrite, arsenopyrite, boulangerite, chalcopyrite, grey ores, and bournonite. Gangue minerals are represented by quartz, ankerite, siderite, and dickite.

The parageneses, which taken all together form all the polymetallic veins of the Nagol' Ridge, form at temperatures of $150\text{--}400^\circ\text{C}$ and pressures of $500\text{--}1700$ atm. The composition and thermobaric conditions of formation of mineral assemblages correspond to their stratigraphic position. That having the highest temperature ($250\text{--}400^\circ\text{C}$), the Bobrikovsk arsenic-polymetallic ore show, occupies the lowest stratigraphic position, suites $\text{C}_1^4\text{--}\text{C}_1^5$. The relatively moderate-temperature ($180\text{--}300^\circ\text{C}$) Nizhnenagol'chansk polymetallic ore show is located in the upper beds of suite C_1^5 . The lowest-temperature ($150\text{--}250^\circ\text{C}$) deposit, the Esaulovsk, a polymetallic deposit with sulfosalts, is restricted to suite C_2^1 . If we add that the Verovsk arsenic ore show located on the Main Anticlinal west of the Nagol' Ridge is localized in the rocks of suite C_2^2 , and the Nikitovsk mercury deposit is localized in suites $\text{C}_2^2\text{--}\text{C}_2^3$, then the change from northwest to southeast of the relatively low-temperature and more shallow deposits to higher temperature, deeper deposits becomes clearly visible. In the same direction and from the northern to the southern boundaries of the Donbass to the center the degree of metamorphism of the coal rocks regularly increases. While in the west the coals and rocks are at the catagenic stage of development (coals of grades D, G, Zh, K, and OS), those in the southwest are of metagenic stage (coals of grades T, PA, and A). From the data presented above it follows that the stratigraphic positions of the different ore assemblages, their conditions of formation, the metamorphism of the host rocks and coals are closely interrelated by the thermodynamic environment of the host sequence, which left its imprint in the

parallel of the changes of the factors mentioned. If this hypothesis is correct, then we are justified in applying the methods of paleohydrological reconstruction to the Donets Coal Basin, which in the course of its long history has undergone elisional and infiltrational stages of development.

During the elisional stage (Carboniferous-Lower Permian) continuous short-cycle accumulation of a sequence of primarily carbonaceous-argillaceous sediments together with the major ore-forming elements occurred, these being in different forms and states (mechanical admixtures, sorbed, or as compounds). The gradual accumulation at great depths with short hiatuses helped increase the hydrostatic and lithostatic pressure and contributed to the strong heating of the water of sedimentation and the expressed pore solutions. As a result of this, at the deep horizons a basin of underground mineralized waters formed, the movement of which was hindered, since the section consisted of clay-rich rocks practically impermeable to water.

The original compositional zoning of these solutions due to the vertical zoning of the thermodynamic environment and coinciding with the metamorphic zones of the rocks and the coals corresponds to the hydrochemical profile of the underground waters in bituminous rocks [5]. These deep waters are usually enriched in Pb, Zn, Cu, Li, and other elements, even where these metals are at their Clarke levels in the rocks. Since the concentrations of ore elements in the host rocks of the Nagol' Ridge are several times their Clarke levels [7], it is natural to expect that in the underground waters they will also be found in elevated amounts.

The horizontal hydrochemical zoning of the subsurface waters of the Donbass is in agreement with the above noted metamorphic zoning. From the northwest to the southeast there is a regular change of the bicarbonate-calcic and bicarbonate-sulfate-calcium waters to sulfate-sodium, sulfate-chloride-sodium and chloride-sodium waters [6].

Infiltrational Stage. At the end of the Paleozoic, sedimentation ceased, and descending movements were replaced by ascending. Along with fold formation, faulting and jointing began, immediately improving the conditions for the formation of subsurface solutions, especially at the intersections of structures trending in different directions (normal-trending arches). The formation of large-scale fissures and arches was due to the irreversible adiabatic expansion of solutions and their mixing with meteoric waters, which in turn resulted in the precipitation of the ore components.

The hypotheses of the mechanism that formed the polymetallic veins of the Nagol' Ridge are completely reflected in the genetic features of both the ore and gangue minerals. The effect of the irreversible adiabatic expansion, thus the low degree of heat and mass exchange between the hydrothermal solutions and the country rock accounts for the weak development or absence of metasomatites about the ore veins. According to the data of P. Sh. Tulmin and S. P. Clark [17], the major role in the precipitation of ore elements during adiabatic expansion is played not so much by cooling as by the fall in pressure, which allows the solutions to boil.

A thermobarogeochemical study of the minerals of the ore veins (Table 2) showed that a major component of the inclusions is carbonic acid. It is found in gas and fluid inclusions, confined to the liquid phase. From the overall state and degree of saturation of CO_2 , the hydrothermal solutions can be ranked in the following order on the basis of the data obtained from the study of their fluid inclusions: homogeneous water-carbonic acid fluid; heterogeneous boiling medium; homogeneous weakly saturated CO_2 solution.

The wide distribution of iron-magnesium carbonates (siderite and ankerite) in the ore veins and the absence of calcite is explained by just this high partial pressure of CO_2 in the hydrothermal system. The formation of the water-carbonic acid fluids occurred in regions where faulting and doming occurred as a result of oxygen-rich meteoric water penetrating to the depths of the sedimentary sequence. This in turn lead to the oxidation of the gases produced by the metamorphic alteration of the carbonaceous strata (CO_2 , CH, etc.) and the formation of carbonic acid.

The results of the study of the carbon isotope composition (Table 2) showed that the $\delta^{13}\text{C}$ values of the vein carbonates are close to the isotopic composition of the carbon of carbonic acid in the fluid inclusions ($\delta^{13}\text{C} = 5.0$ to $-11.8^\circ/\text{‰}$) and of carbonic acid gas in modern mines ($\delta^{13}\text{C} = -8.7$ to $-9.0^\circ/\text{‰}$) [1, 9]. The source of carbon having this isotopic

TABLE 2. Some Mineral Parageneses, Their Formation Conditions, and Carbon and Oxygen Isotope Compositions in Ore Veins in the Nagol' Ridge

Ore show or deposit	Paragenetic assemblage	Mineral	Formation temp., °C	Pressure, atm	Solution concn., %	Composition of gases, cm ³ /kg				$\delta^{13}\text{C}$ of carbonates ‰ (PDB)	$\delta^{18}\text{O}$ of carbonates ‰ (SMOW)
						CO	CH ₄	H ₂	CO ₂		
Bobrikova	Quartz + siderite + arsenopyrite + pyrite + sphalerite + galena	Quartz	253—403	1050—860	2,5—5,8	74	4	20	316	—	—
		Sphalerite	344—356	1500—1700	2,0—9,8	—	—	—	—	—	—
		Siderite	271—300	1250—800	3,5—8,0	—	—	—	—	—1,6 ± —4,8	—22,8 ± —27,8
		Quartz + ankerite + galena + bournonite	250—275 247—260	1000—800 900—750	4,5—5,7 3,0—5,5	32 —	7 —	— —	76 —	— —9,4	— —
Ostryi Bugor	Quartz + siderite + pyrite + arsenopyrite	Quartz	300—310	1300—1000	3,5—7,0	12	15	10	112	—	—
		Siderite	285—293	1000	4,8—6,5	—	—	—	—	—5,8	—14,5
Nizhni Nagol'nik	Quartz + ankerite + sphalerite + galena	Quartz	215—235	850—700	2,5—5,0	20	1	—	32	—	—
		Sphalerite	254—275	1050	2,0—6,7	—	—	—	—	—	—
		Ankerite	190—205	800	—	—	—	—	—	+1,8	—16,7
Esaulovka	Quartz + ankerite + sphalerite + galena + boulangerite	Quartz	215	700—550	5,0—5,5	15	4	20	15	—	—
		Ankerite	150—195	480—550	2,6—4,0	—	—	—	—	—3,1	—14,3

Note. The temperatures of formation were determined by the homogenization method of fluid inclusions in quartz, carbonates, and sphalerites. The pressure was measured from the density of the carbonic acid in the fluid inclusions. The analysis of the gas composition was performed on an LKhM-8MD chromatograph. The analyst was L. F. Passal'skaya. The isotopic composition of the carbon and oxygen was determined at the Stable Isotope Geochemistry Department of the Division of Metallogeny of the IGFM of the Academy of Sciences of the Ukrainian SSR. The analysts were F. I. Berezovskii and I. Z. Korostyshevskii.

composition could be either the carbonates of the country rock ($\delta^{13}\text{C} = 2.5$ to -5.1‰) or the gaseous products of the metamorphic alteration of organic-rich strata.

At the present time it is not possible to evaluate quantitatively the role of the carbonate and the organic carbon. However, judging from the values of the isotopic composition of the carbon of the ankerite and siderite of the ore veins ($\delta^{13}\text{C} = +1.8$ to -9.4‰), the organic component of the carbon played a distinctly subordinate role. At the same time the amount of organic carbon in the hydrothermal solutions decreases with distance from the tectonic disturbances, as evidenced by the increasing isotopic heaviness of the carbon of the vein carbonates and the carbonic acid in the fluid inclusions away from the arches of the anticlinal structures [9].

The enrichment of the ore vein carbonates in the light isotope relative to the carbonate carbon further from the tectonic disturbances is associated with the fractionation of the carbon isotopes as the iron-manganese carbonates form at elevated temperatures and pressures and with the addition of CO_2 to the hydrothermal solutions from oxidized organic matter.

The isotopic composition of the oxygen ($\delta^{18}\text{O}$) of the carbonates varies from 14.3 to 27.8 ‰ , with the highest-temperature carbonates being enriched in the heavy isotope. The $\delta^{18}\text{O}$ values given are characteristic of metamorphic solutions diluted with meteoric waters [16]. The significant dispersion in the $\delta^{18}\text{O}$ values suggests that the system was relatively open to oxygen exchange during of mineral formation, as well as that there was a considerable amount of meteoric water in the system, especially during the low-temperature stages of mineral formation.

Evidence supporting the meteoric-metamorphic hypothesis for the formation of the ore veins of the Nagol' Ridge is the similarity of the mineralizing solutions preserved in the fluid inclusions and the subsurface waters of the center of the Donbass region [6]. Both are characterized by a bicarbonate-chloride-sodium salt composition, a low concentration (5-10%) of dissolved components, give an acid response (pH 7.0-8.8), have an oxygen-nitrogen-carbonic acid gas phase, and elevated concentrations of Li.

Other typomorphic characteristics of the sulfide mineralization of the Nagol' Ridge should also be noted: 1) the variable chemical composition of the ore minerals, where the same elements may occur as either anions or cations, depending on the thermobaric conditions; 2) the heterogeneous internal structure of ore minerals having a large quantity of microinclusions in the form of decomposition products of solid solutions and epitaxial overgrowths; 3) a sulfide sulfur isotopic composition close to the meteoric standard.

* * *

Analysis of the patterns of sulfide ore formations in the sedimentary formations of the Ukraine has shown that mineralization occurred in strict accordance with the stages of post-sedimentary alterations due to the processes of diagenesis, catagenesis, and metagenesis. Each process has its corresponding genetic ore type with its characteristic thermodynamic conditions of formation, specific minerals, structural and textural peculiarities, isotopic and geochemical characteristics, and other properties.

The occurrence and composition of the paragenetic assemblages of the ore minerals is predetermined by the primary chemical composition of the sediments and the stages of their post-sedimental alteration. An important role in the processes of cata- and metagenic ore formation is played by metamorphic solutions and meteoric waters.

The genetic features of the sulfide mineralization considered here in conjunction with geological evidence can serve as important mineralogical criteria in assessing the ore-bearing prospects of metasedimentary formations.

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CLASSIFICATION OF CHLORITES ON THE BASIS OF X-RAY
DATA WITH SPECIAL REFERENCE TO PALEOZOIC ROCKS
OF DIFFERENT AGES IN THE TIMAN-PECHORA PROVINCE

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UDC 549.623.7:551.73(470.1)

Based on x-ray patterns of sediments of different ages from the Timan-Pechora Province, a classification of chlorites is constructed and their crystallochemical formula is calculated. A linear relation has been established between ferruginosity and the parameter b . The uses of the classification for genetic reconstructions are indicated.

Studies of the clay fractions of sediments with x-ray powder patterns in the exploration for oil and gas indicate the wide structural variety of chlorites contained in the clay fraction. The chlorites differ in ratios of intensities of even and odd orders in oriented air-dry preparations and respond differently to saturation with organic liquids and to heating.

Variations of two parameters have been used to classify these wide varieties of chlorites: the ferruginosity and the aluminum-for-silicon substitution index [11].

The calculations were based on an idealized formula of chlorite: $(\text{Mg}_{6-x-y}\text{Fe}_y\text{Al}_x) \cdot (\text{Si}_{4-x}\text{Al}_x)\text{O}_{10}(\text{OH})_8$. By the variation of ferruginosity $K_{\text{Fe}} = \text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg}^{2+})$, three types of chlorites are distinguished: magnesian, magnesian-ferruginous, and ferruginous varieties (the ferruginosity is equal to 0-0.25; 0.25-0.75; 0.75-1.0 respectively).

The gross iron content (y) was calculated according to the linear relation proposed by Shirozu [12]: $b = 9.21 + 0.037 y$. The parameter b was found by the position of the reflection 060, determined by x-ray oblique structures [7]. The contents of trivalent cations (x) was estimated with the Kepezhinskas equation: $d_{001} = 14.648 - 0.378x$ [5]. The exact value of d_{001} was calculated from reflections of the 10th and 12th orders.

The results of the calculations are given in Table 1. Even in a small collection of specimens, ferruginosity varies in a broad range and covers the three chlorite varieties.

According to the chloride classification system suggested by Foster, the series of limiting Al-for-Si substitution values between 2.34 and 3.45 was divided into three intervals (2.35-2.75; 2.75-3.10; 3.10-3.45); combining these with the groups of the chlorites based on ferruginosity, we obtain nine fields (Fig. 1). As with Foster, all of our chlorites fell mainly within five fields.

It was not always possible to obtain all the parameters for a calculations of crystallochemical formula and ferruginosity. In some instances only the 060 reflection could be read. For the classification of these chlorites K_{Fe} was plotted versus b (Fig. 2). The clear linear correlation between these two values makes for an easy evaluation of ferruginosity and a simple classification of chlorites.

This classification is more informative and helps resolve the problems of chloride genesis with more confidence. It is known, for example, that gross aluminum content in octahedra and tetrahedra gives information about the origin of chlorites: the value is always greater than 2.2 in chlorites of a primary sedimentary origin [6].

We superimposed on the chlorite distribution diagram after Foster (Fig. 1) the diagram proposed by Kossovskaya and Drits, which reflects the genesis of chlorites. The diagram

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Translated from *Litologiya i Poleznye Iskopaemye*, No. 5, pp. 70-77, September-October, 1987.
Original article submitted May 20, 1986.

TABLE 5. Classification of Chlorites by X-Ray Patterns

Specimen number	Specimen collection interval, m	Age	Rock	d_{001} , Å	b, Å	x(Al ³⁺)	y(Fe ²⁺)	KFe	Chlorite type
1116	2997,0—3000,0	O ₁	Argillite	14,23	9,22	1,10	0,32	0,06	Magnesial
1111	2230,0—2237,0	D ₃	Sandstone	14,19	9,22	1,21	0,32	0,07	
55	1565,0—1571,3	P ₁		14,21	9,23	1,16	0,65	0,13	
519	2862,0—2865,0	O ₁	Argillite	14,20	9,23	1,20	0,60	0,13	
700	3101,0—3109,0	»		14,16	9,25	1,29	1,14	0,24	
396	1776,4—1782,4	D ₃	Clay	14,18	9,25	1,23	1,14	0,24	
S	1512,2—1519,0	P ₂	Siltstone	14,12	9,25	1,39	1,14	0,25	
214	1592,1—1596,9	P ₁							
300*	2137,9—2151,8	»	Sandstone	14,22	9,26	1,13	1,45	0,29	Ferruginous-magnesial
238	2000,0—2012,0	»	Siltstone	14,21	9,26	1,16	1,46	0,30	
780	1249,0—1260,2	T ₁	Sandstone	14,23	9,26	1,10	1,46	0,30	
1034	3603,0—3609,0	O ₁	Shale	14,15	9,26	1,32	1,46	0,31	
1113	1853,0—1860,0	P	Argillite	14,17	9,27	1,26	1,62	0,34	
C*	1242,0—1247,5	P ₂	Sandstone	14,32	9,27	0,88	1,78	0,35	
111*	1680,6—1686,0	»	»	14,29	9,28	0,94	1,78	0,35	
788	2149,0—2157,0	C?	Argillite	14,18	9,28	1,24	1,78	0,37	
225	1559,5—1564,0	P ₁	»	14,20	9,28	1,20	1,78	0,37	
707	1672,0—1677,0	P ₂	»	14,16	9,28	1,29	1,78	0,38	
1118	2862,8—2865,0	D ₃	»	14,40	9,29	0,66	2,11	0,39	
288	1702,0—1707,4	P ₂	Clay	14,21	9,29	1,16	2,10	0,43	
387	2531,6—2537,1	D ₃	Argillite	14,16	9,29	1,29	2,10	0,44	
830	3203,0—3207,0	C ₁	»	14,15	9,29	1,32	2,11	0,45	
1098	4149,0—4150,4	D ₃	Sandstone	14,12	9,29	1,40	2,16	0,47	
1008	3871,5—3879,8	D ₂	»	14,12	9,29	1,39	2,20	0,48	
1009	3871,5—3879,8	»							
1012	3885,4—3893,4	»	»	14,11	9,29	1,42	2,27	0,50	
1026	3321,0—3329,1	»	»	14,11	9,30	1,42	2,43	0,53	
685	1983,5—1986,8	»	Argillite	14,21	9,31	1,20	2,60	0,54	
1131	3024,0—3032,0	»	Sandstone	14,10	9,30	1,45	2,59	0,57	
974	3658,2—3658,3	»	Siltstone	14,04	9,31	1,61	2,70	0,61	
504	3730,6—3738,8	D ₃	Sandstone	14,13	9,32	1,37	2,91	0,62	
722	3486,0—3498,8	D ₂	Clay	14,10	9,32	1,45	2,97	0,65	
1069	1924,0—1932,8	D ₃	Argillite	14,10	9,32	1,45	3,08	0,67	
641	2255,0—2263,0	»	Sandstone	14,10	9,33	1,45	3,24	0,71	
647	1947,0—1955,0	D ₂	Siltstone	14,15	9,34	1,32	3,40	0,73	
1130	3021,0—3024,0	»	Sandstone	14,14	9,34	1,34	3,40	0,73	
767	2995,3—2999,4	D ₃	Argillite	14,12	9,34	1,39	3,40	0,74	
771	3070,4—3073,9	»	Clay	14,10	9,34	1,45	3,40	0,76	Ferruginous
768	3007,4—3012,0	»	Argillite	14,10	9,34	1,45	3,40	0,76	
640	2218,0—2226,0	»	»	14,16	9,35	1,29	3,73	0,79	
669	2933,0—2936,8	»	»	14,10	9,35	1,45	3,73	0,82	

shows that chlorites from graywacke samples (marked by an asterisk in the table) are in the field of primary magmatic rocks: the gross aluminum content is below 2.2. All the other chlorites are above the line of 2.2; ferruginous chlorites in the field of iron ore formations; ferruginous-magnesial chlorites are in the field of terrigenous formations; and magnesial chlorites are in the field of chlorites from ultrabasic or dolomite-gypsum formations. Only two magnesial chlorites fell outside all the fields.

The fields of magnesial chlorites of dolomite-gypsum formations contain two specimens. The first specimen (sample 1111) was collected from the top of the Kinov-Sargaev (D₃) regional cover; the other specimen (sample 55) was taken at the base of a large Permian terrigenous sedimentary cycle.

Most specimens in a broad stratigraphic interval were in the field of ferruginous-magnesial chlorites of terrigenous formations. Recent studies have shown that terrigenous sediments are series of laterally consecutive large lenses reflecting the sedimentary cycle of the section. Ferruginous-magnesial chlorite samples obviously belong to different parts of the profile of regressive sedimentation.

Other chlorites exhibit parts of the profile of regressive sedimentary features.

From the position of the specimens in the section and the microscopic characteristics of the rocks we determine that all the chlorites in the field of iron ore formations are confined to interruptions in sedimentation. In particular, sample 771 (Table 1) was collected from the base of the Kinov-Sargaev bed just a few meters above a washed-out surface of terrigenous rocks; sample 768 contained ferruginous oolites; sample 669, fragments of effusive

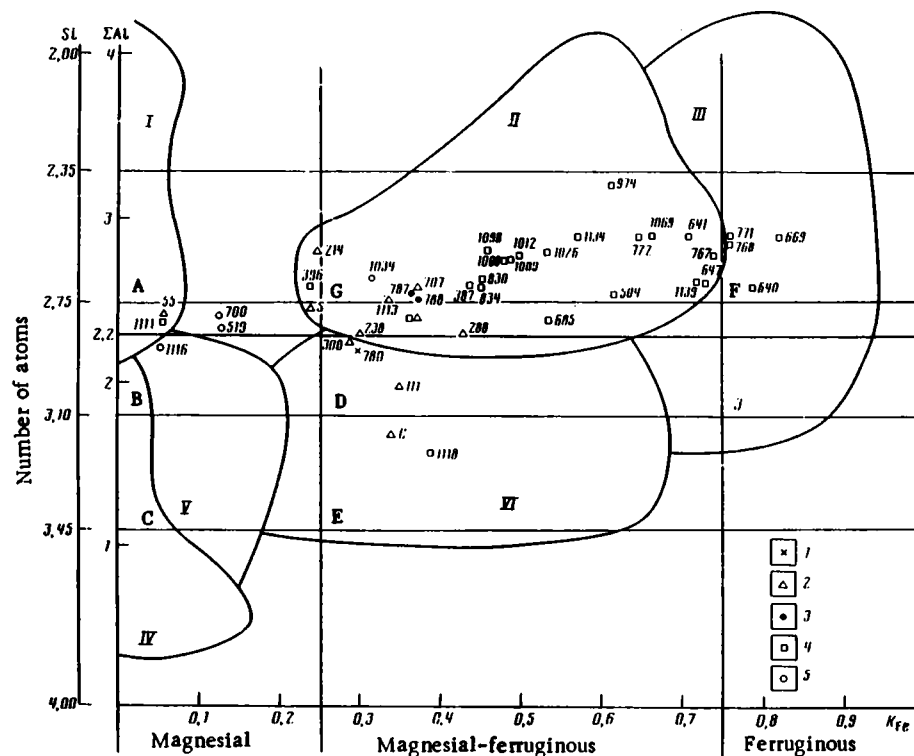


Fig. 1

Fig. 1. Crystallochemical characteristics of chlorites. Fields fter Kossovskaya and Drits [6]: (I) magnesian chlorites of dolomite-gypsum formations; (II) ferruginous-magnesian chlorites of terrigenous formations; (III) ferruginous chlorites of iron ore formations; (IV) magnesian chlorites of serpentinites; (V) magnesian chlorites of ultrabasites; (VI) ferruginous magnesian chlorites of andesite-basalts. Fields (squares) after Foster [11]: (A) sheridanite; (B) clinocllore; (c) pennine; (D) ripidolite; (E) brunsvigite; (F) diabantite; (G) turingite; (H) chamosite. (1-5) age of rocks (1 - Triassic, 2 - Permian, 3 - Carboniferous, 4 - Devonian, 5 - Ordovician).

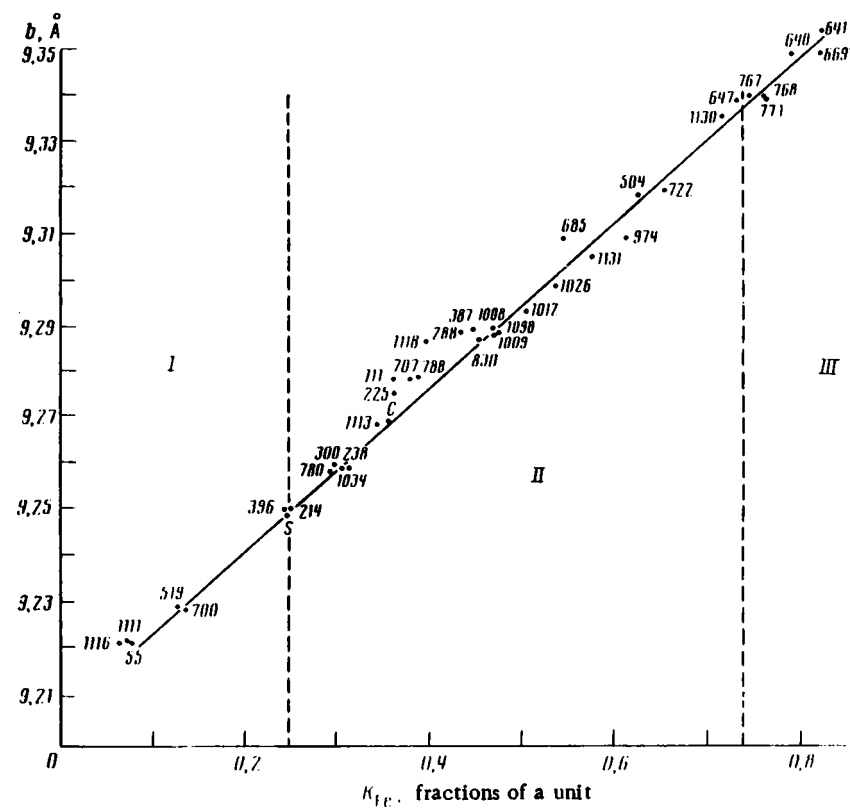


Fig. 2

Fig. 2. Ferruginosity K_{Fe} versus the parameter b . Chlorites: (I) mangesian; (II) magnesian-ferruginous; (III) ferruginous.

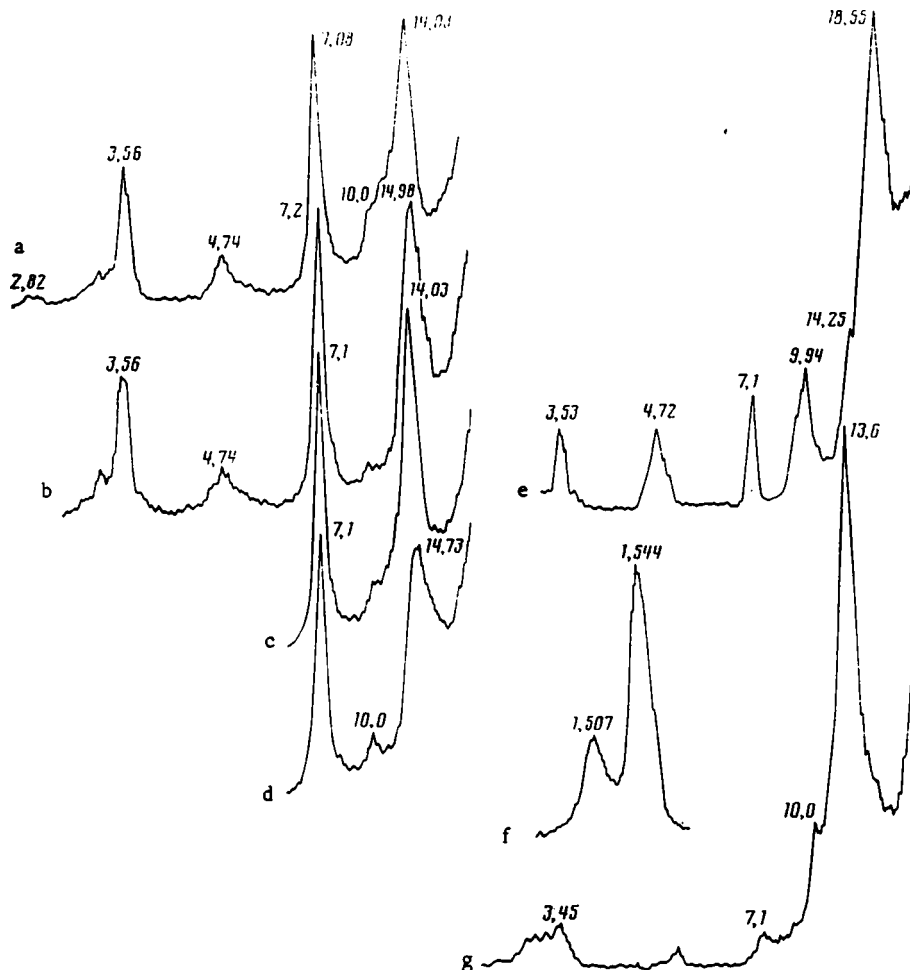


Fig. 3. Diffractograms of siltstone clay fraction (hole 77, depth 1792.6-1798.0 m): (a) natural air-dry specimen; (b) treated with ethylenglycol; (c) after one cycle of HS and DMSO treatment; (d) same, after two cycles; (e) same, after three cycles; (f) heated at 500°C for 1 h; (g) reflection 060.

rocks; sample 640 was collected from almost the very top of the Kinov horizon. The description of the core in that interval notes the presence of tuffogenic material.

Four of the five specimens that fell into the field of ferruginous-magnesian chlorites of andesite-basalts occur in the section on distinct boundaries between sedimentary and tectonic beds. Sample 780 was taken from the roof of sandstones of the Charkobozhskaya suite, which marks the beginning of the Lower Triassic. Sandstones contain a gravel admixture and often conglomerate interlayers. Sample C was taken from the roof of the terrigenous Permian section. Variegated purple and green rocks are present in the core from this interval; all polished sections contain fragments of schists, chloritized fragments of effusive rocks, and tuffogenic material. Sample III is taken from the roof of a thick basal bed at the base of the Upper Permian. The last sample (1118) is from the Kinov-Sargaev regional cover. The field of ultrabasic chlorites contains one sample (1116) from the base of the Lower Ordovician terrigenous stratum.

Outside the fields identified by Kossovskaya and Drits were two specimens of terrigenous Ordovician rocks: sample 519 (a red sandstone) and sample 700 (a red argillite).

Almost all the specimens tend to occur in section intervals characterized by invigoration of tectonic activity and magmatism. Distinct correlations in the diagram are apparently due to similar composition of the parent material and similar chloritization processes.

Diagnosis of small amounts of kaolinite when mixed with chlorite in a fraction is known to be extremely difficult. An intercalation of preparations with hydrazine (HS) and dimethylsulfoxide (DMSO) is done sometimes to separate the superimposed reflections of these minerals; as a result the kaolinite reflections are shifted to 11.2 and 3.7 Å, and chlorite reflections remain in the same position [1, 2, 9]. We used this technique to determine the features of chlorite swelling after ethylene glycol saturation to 14.98 Å. Specimens from Permian terrigenous beds of the Khar'yaga area (site 77 Khar'yaga, interval 1792-1798 m; Fig. 3a, b) were treated with HS and DMSO. Saturations were done in cycles; the preparations were first placed in exsiccators for a day and treated with HS vapors and then with DMSO vapors.

After a single saturation cycle no changes were observed in the diffractogram; the mineral behaved as ordinary chlorite (Fig. 3c). After the second saturation a "tail" appeared at the 14 Å peak or small angles (see Fig. 3d); after the third cycle, reflections of two phases were distinct: magnesian chlorite and intercalated montmorillonite (montmorillonite produces reflection of 18.5 and 9.2 Å upon intercalation; Fig. 3e).

The petrographic investigation of this sample showed several modifications of chloride in the rock (coarse-grained polymictic siltstone). Clastic chlorite consists of green, greenish-brown, and brown slightly pleochroic grains interfering in gray-bluish and bluish-gray shades. It has an aggregate extinction, sometimes uniform. Grains with abnormally blue pigmentation (pennine) or virtually isotropic grains are also found.

Brownish-green pleochroic chlorite with cleavage traces and zonal extinction in golden and blue shades develops after biotite. Biotite flakes are adjusted to the harder surrounding grains.

Of most interest is chlorite developed on endings of long fibrous bodies formed by identically oriented organomineral clay material. In transmitted light the bodies are light-brown with brownish-greenish pigmentation at the endings; the interference color ranges from golden-yellow and brownish-yellow to orange. The bodies are typical relicts of plant root systems, indicating the ancient soil origin of this rock. Pyrite is often developed after such roots.

The original material of these bodies was probably montmorillonite (golden-yellowish shades in crossed nicols); it was followed by highly dispersed secondary matter (the parallel placement of particles with simultaneous extinction); finally, during diagenesis catagenesis it became chloritized. All the stages of transition from montmorillonite to chloride can be observed in polished sections. Montmorillonite, in turn, could be formed during the soil development after pyroclastic material that is often found in Permian sediments or in degradation of clastic chlorite unstable in acid soil conditions. A similar situation has been discussed in [8] with special reference to fossil soils of the Carboniferous in Donbass.

Generalizing the data of x-ry and petrographic investigations, we concluded that a cyclic saturation with HS and DMSO elicited in chlorites the so-called structural memory, so that chlorite formed after montmorillonite became capable of swelling to the original (montmorillonitic) framework.

The reflections of magnesian chlorite can be interpreted as belonging to chlorite developed after biotite, because the particles of detrital chlorite are usually larger than 1 μm and are not part of the clay fraction.

All this refers to trioctahedral chlorites. Dioctahedral chlorites are much less frequent in Timan-Pechora sediments and have specific features of their own. A dioctahedral chloride from the Triassic of the province was for the first time described in detail by Sakharov and Khlybov [10]. They believed it to be a deficient dioctahedral chlorite with a structure consisting of imperfect gibbsitelike layers and pyrophyllitelike layers whose tetrahedral frameworks have an insular structure (Fig. 4, II). In the Triassic, chlorites of this kind are typical for ancient soils and are their indicators.

In our studies we observed two varieties of dioctahedral chlorites: with soil chlorites similar to the variety mentioned earlier (Fig. 4, I) and ordinary dioctahedral chloride described by Brindley [2] (Fig. 4, III) formed by superimposed hydrothermal processes. Such chlorites are found in the Lower Devonian and older sediments of the province. All the chlorites of Fig. 4 have $d_{000} = 1.492-1.495\text{Å}$, indicating that they are dioctahedral. They do not swell with ethyleneglycol and are not destroyed by 10% hydrochloric acid in a water for 2 h. After being heated to 550°C for 1 h, however, they behave differently (Fig. 4b).

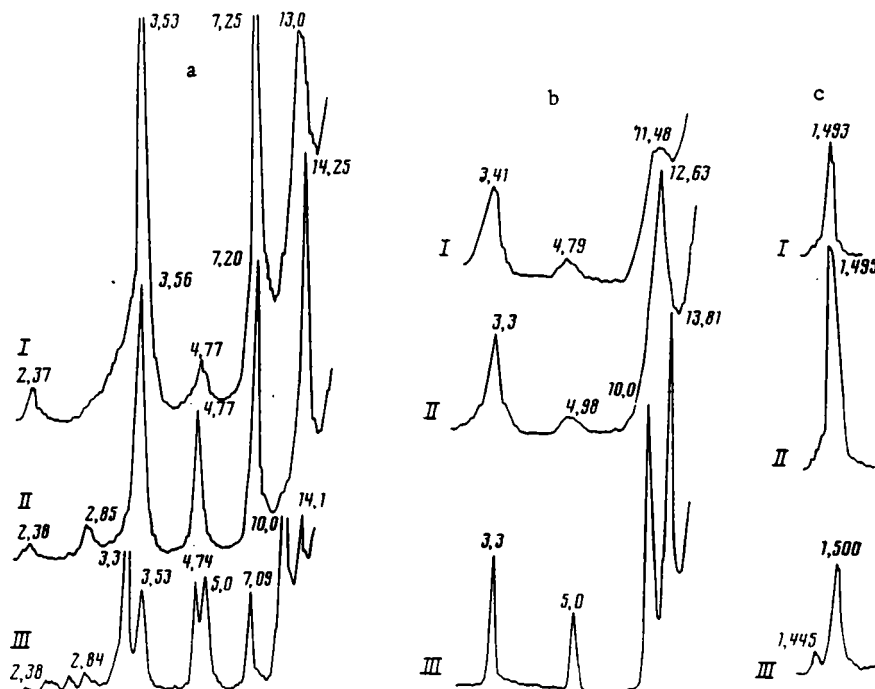


Fig. 4. Diffractograms of dioctahedral chlorites: (I) samples 63 (hole 5, depth 262-267 m); (II) sample from exposure 71 (Greater Synya River); (III) sample 66 (hole 1, depth 2879-2886 m); (a) air-dry preparations; (b) heated to 550°C for 1 h; (c) reflection 060.

While in the first specimen, broad diffuse maxima at 11.48; 4.79; 3.41 Å, are observed, in the second the reflection 001, although wide, has a distinct maximum of 12.63 Å; in the third specimen a clear reflection with $d_{001} = 13.81$ Å is seen; the latter's intensity is obviously increased compared to the air-dry state and reflections of higher orders have disappeared. The intensity of the 003 reflection is remarkable. Judging by the literary data, it should be greater for dioctahedral chlorites than in other reflections. In our case, however, this was not always so (Fig. 4a, b). The relative intensities and the behavior of dioctahedral chlorites upon heating seem to reflect a multitude of modifications similar to that in the group of trioctahedral chlorites.

The recordings were made on DRON-3 equipment in copper radiation with a plain graphite monochromator on a diffracted beam and four slots (1, 0.5, and 0.5 mm) according to the method developed by the Mineralogy Department of Kazan University. This method greatly improved the intensity of reflections and enhanced the sensitivity of the procedure.

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Rb/Sr AND K/Ar-AGES OF GLOBULAR LAYER SILICATES
FROM THE RIPHEAN AND CAMBRIAN OF THE USSR: DATA
IN THE EVALUATION OF AGE-DATED SUBSTANCES

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UDC 550.93:549.623:551.732

Results of Rb/Sr and K/Ar-dated, mineralogically thoroughly studied, globular, 2:1 layer silicates (glauconite, Al-glauconite, illite, and their structural varieties), obtained from Lower Cambrian (Estonia and E. Siberia) and Upper Proterozoic (S. Ural, E. Siberia) sediments are discussed. A dominant portion of the received isotope dates, including Rb/Sr and K/Ar dates, are too young when compared with the stratigraphic age of the corresponding deposits. There is no unequivocal correlation between the degree of stability of isotope-dating systems, the degree of structural perfection and the ratio of expandable layers. Differences have been noted in the Mössbauer spectra of minerals; these reflect stratigraphically anticipated and "rejuvenated" isotope ages. The possible geological reasons for the breakdown of isotopic-geochronological systems in the dated material are reviewed and it is shown that these reasons defy a single, uniform interpretation.

Globular dioctahedral 2:1 layer silicates (glauconite, Al-glauconite, and illite) are among the few sedimentary substances used in age dating; theoretical applicable for K/Ar and Rb/Sr age dating methods. Actual dating of these substances showed that, in addition to dates expected from the stratigraphic positions of the dated samples, a significant number of anomalous (mostly too young) dates were only obtained. Various samples from the same unit and even various fractions of the same sample often displayed a significant date-scatter (survey data and bibliography: in publications [14, 20, 26, and 49]). Increased (older) isotope dates, with rare exceptions, occurred only in Mesozoic-Cenozoic samples, usually associated with radioisotope remnants from preexisting minerals, in conjunction with their transformation. Sometimes they formed during problematic process of glauconite globule-reworking from older into younger sediments. As far as the reduced isotope ages are concerned, they were related to the destruction of the isotope systems in minerals, due to different processes as diffusional loss of radioisotopes from the crystal lattice, loss of and Rb to the outside medium during diagenesis and katagenesis, ion-exchange reactions, or the combinations of these factors.

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Regardless of the suggested relative ease of the destruction of the isotope system of the studied minerals, attributed to crystallochemical characteristics, the data suggest that the measured isotope ratios in these minerals may be expressed not simply as the result of the destruction of isotope systems, apart from geological considerations, but associated with specific geological events of the past. Essentially, detable substances that we are interested in often retaining the isotope "memories" of geological events of the distant past, under conditions of such superimposed effects as deep burial of the enclosing beds, accompanying heating, subsequent folding and rarely, also overthrusting. The most representative in this respect are the Riphean deposits of the Baikallides in the Yenisei Ridge, the Hercynides of the Ural Mts. and the Laramides of the Rocky Mts., USA where dated globules retained Late Cambrian values of isotope dates [6, 29, 46].

The above data raises pertinent questions about the reliability of these dated substances and about the relationships between stages of closing and destruction of their isotope systems, associated with actual events in relation to basic regional geological findings [7, 21, 33, 43, 45, 47, 49, etc.]. These questions usually are resolved in the contemporary literature on the basis of a search for correlated relationships between mineralogical and crystallochemical characteristics of specific samples and based on the degree of stability (destruction) of their K/Ar and Rb/Sr systems. Study of the Mesozoic-Cenozoic West European glauconites led to the formulation of characteristics, required of minerals to be dated: globular shape of the minerals, relatively large globule size, absence of visible traces of secondary alterations, high density and paramagnetic susceptibility, high degree of structural perfection (polytype 1M), small number of expandable layers, and importantly: a relatively high K content ($K_2O \geq 7\%$). K plays a dominant role in the perfection of the mineral structures [45, 47, 49].

The fulfillment of these requirements in a number of instances led to a significant reduction in the scatter of the isotope dates from Mesozoic glauconites. In other instances, however, the requirements were not necessary for obtaining stratigraphically anticipated K/Ar and Rb/Sr dates from these minerals.

Nikolaeva [20] has studied a large number of glauconite group mineral samples of various ages. She found that one of the major criteria in selecting substances for age-dating requires comparison of the chemical composition with the statistical average value; recommending elimination of such samples in which the element ratio does not correspond to the typomorphic composition, typical of "unaltered" samples from uniform of formations. The advisability of the use of the statistical approach in the problems involved is not an issue here. Among the ancient, Lower Cambrian and Precambrian minerals entirely unaltered ones were absent. It is impractical to exclude all altered samples from geochronological consideration.

These contradictions emphasized the insufficient nature of available empirical data in obtaining a model for the behavior of K/Ar and Rb/Sr isotope systems in glauconite minerals during katagentic and diagenetic stages. The point is that most available information in the literature on isotope ages is based only on the K/Ar method, without mineralogical studies of the dated matter. In certain instances these minerals had a very low K-concentrations. At the same time, the cited age-dated substances remain the main source of isotope age data for the Cambrian, Vendian and Riphean deposits of the USSR. The purpose of this paper is to provide new Rb/Sr and K/Ar dates through crystallochemically studied globular diocahedral 2:1 layer silicates, obtained from Riphean and Cambrian reference sections of the USSR and to consider possible reasons for the decomposition of their age-dating isotope systems.

Three structurally isomorphic series were established among these silicates: glauconite $\rightarrow$ glauconite-smectite; Al-glauconite $\rightarrow$ Al-glauconite-smectite; and illite $\rightarrow$ illite-smectite. Low-charge micas, illites and mixed-layer minerals form among them. Among them, illite, according to the International Committee on Nomenclature [35] is defined as a nonexpandable micaceous mineral, with an ideal crystallochemical formula of $K_{0.75}Si_{3.5}Al_{0.5}Al_{1.75}R_{0.25}^{2+}O_{10} \cdot (OH)_2$.

Stratigraphic Position of the Studied Samples. The studied minerals occur in Lower Cambrian Estonian deposits and along the middle course of the Aldan River, in Upper Riphean type sections of the S. Ural, and in the Upper, Middle, and Lower Riphean of the Siberian Riphean hypostratotype; the section of the Ural-Maisk region. The stratigraphic description of the corresponding units is found in several works [27, 28, 29, etc.].

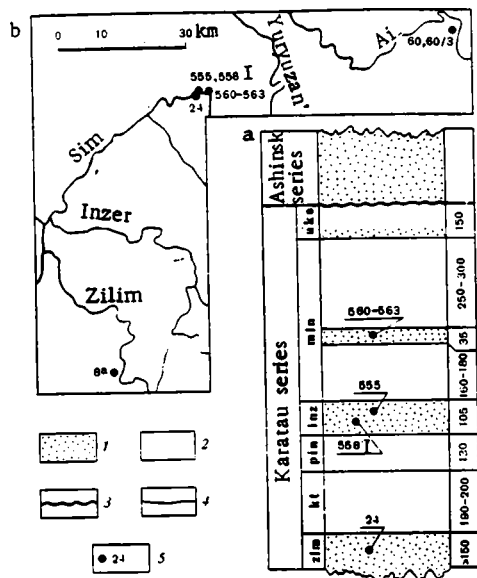


Fig. 1. Upper Riphean and Vendian sequence along the middle reach of the Sim River (a) and locations of the studied samples (b): 1-2) dominant composition or rocks (1 - terrigenous; 2 - carbonate); 3) erosional and stratigraphic unconformities; 4) conformable stratigraphic boundaries; 5) sample location and number. Formation symbols: zlm - Zil'merdaksk; kt - Katavsk; pin - Podinzersk; inz - Inzersk; min - Min'yarsk; uks - Uksk.

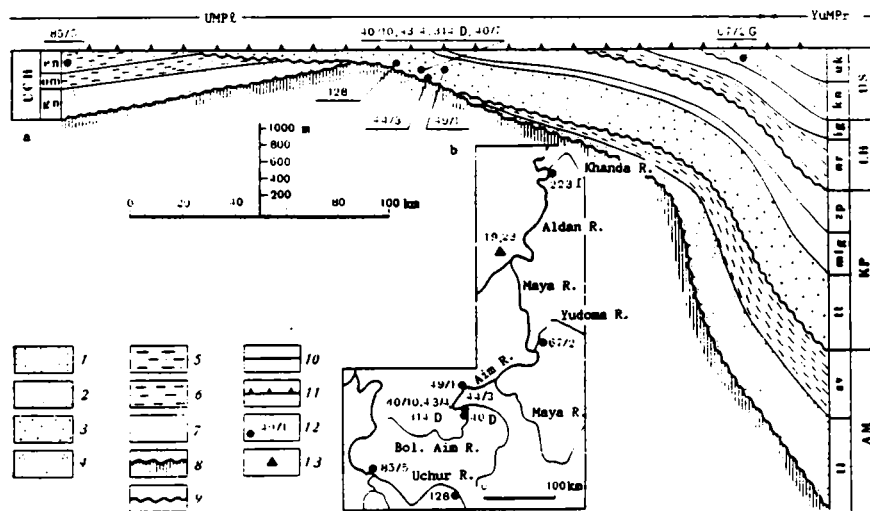


Fig. 2. Generalized paleogeographic profile of Riphean deposits in the southern Uchur-Maisk region at the beginning of the Vendian (Yudomsk) time (a) and geographic positions of the studied samples (b). Rock composition: 1-4) terrigenous (1 - Gonamsk; 2 - Talynsk; 3 - Tottinsk Formation; 4 - Uisk Series); 5) carbonate-terrigenous; 6) terrigenous-carbonate; 7) carbonate; 8) pre-Riphean formations; 9) erosional and stratigraphic unconformities; 10) conformable stratigraphic boundaries; 11) regional pre-Yudomsk unconformities; 12) samples location and number; 13) location of the Mokuisk parameteric (stratigraphic test?) drillholes; Formations: gn) Gonamsk; om) Omakh-tinsk; en) Enninsk; tl) Talynsk; sv) Svetlinsk; tt) Tottinsk; mg1) Malginsk; zp) Tsipandinsk; nr) Neryuensk; ig) Ignikansk; kn) Kandyksk; uk) Ust'kirbinsk; Series: UCH) Uchur; AM) Zimchansk; KP) Kerpyl'sk; LH) Lakhandinsk; US) Uisk; UMP1) Uchur-Maisk Platform; YuMP) Yudomsk-Maisk Depression.

Samples from Estonia (samples #2, 3, 5, E-98, MM-11; Table 2) came from the Lyukatisk Formation (Utriya, Kunde, and Mutsametsa sections), part of the Lower Cambrian Atdabansk Stage [28]; the Aldan River samples (#99/9 and 541) from the base of the variegated formation (Ulakhan-Sulugur outcrops). The latter ones come from the lower zone of the Tommotsk Stage that precedes the Atdabansk Stage. The samples were derived from near the base of the Lower Cambrian. For this reason, there is no doubt about their stratigraphic position. The isotope

TABLE 1. Kr-Ar and Rb-Sr Grain Data (sample #60)*. Processed by Ultrasound in Distilled Water

Duration of preparation, min	K, %	⁴⁰ Ar _p , ng/g	Rb, μg/g	Sr, μg/g	⁸⁷ Sr/ ⁸⁶ Sr	Age, 10 ⁶ yrs	
						K-Ar	Rb-Sr †
0	7,20	495	290	16,4	1,3702	789	851
5	7,40	490	291	23,2	1,1681	765	848
10	7,31	478	293	16,7	1,3600	758	843
15	7,43	489	293	20,3	1,2451	761	849
30	7,40	467	298	22,3	1,2072	737	861

*Size: 0.315-0.2 mm; density: 2.6-2.7 g/cm³.

†Original ratio of ⁸⁷Sr/⁸⁶Sr accepted as 0.7090.

ages of the units involved are questionable. Two reasons explain this: first, from the units in question (unless one does not consider unjustified the K/Ar age dating method of bulk samples of clayey Estonian rocks [30], unavoidably contaminated by terrigenous matter) only greatly "rejuvenated" K/Ar glauconite dates are known [22, 30]. Secondly, the present evaluation of the isotope age of the Precambrian/Cambrian boundary, according to various authors ranges between 530-610 Ma, depending on the employed dated substances and their stratigraphic interpretation [31, 48, 52].

Studied samples from the Urals came from various horizons of the Karatau Series of the Upper Riphean, based on the Precambrian stratigraphic system of the USSR. Four samples (#560-563) came from the Zav'yalovsk member of the Min'yarsk Formation, three (#555, 558I, and 8a) from the Inzersk, two (#60, 60/3) from probable Inzersk beds, and one (#24) from the Zil'merdak Formation (Fig. 1). The absolute age of the Karatau Series has been estimated as ranging between 650 ± 50 and 1000 ± 50 Ma [17, 29]. However, this estimate was based on old K/Ar dates from bulk samples of mineralogically not investigated glauconite and gabbro-diabase.

For this reason, these are just rough estimates. Nevertheless, it may be confirmed that even the higher horizons of the series may be appreciably older than 620 ± 30 Ma. On methodological grounds, this is a reliable age for the Lower/Upper Vendian boundary [16, 17].

Twelve Uchur-Maisk region Riphean samples were analyzed by isotope dating methods. One of the (67/2G) came from the lower horizons of the Kandyksk Formation, Uisk Series, eight (40/7, 40/10, 43/4, 44/3, 49/1, 128, 314D, and 223I) from the lower part of the Tottinsk Formation, from the base of the Kerpyl'sk Series, two (#19 and 23) from probable correlatives of this formation in the Mokuisk stratigraphic test well (2013-2035-m-depth interval [9]), and one (#85/5) from the Enninsk Formation of the Uchur Series (Fig. 2).

All geologists include the Uisk Series into the upper part of the Upper Riphean. This is based on the stratigraphic position of the series at the top of the pre-Vendian (pre-Yudonsk) section in this region, analysis of discordant age dates from a central-type [27] intrusion that cuts through the unit. In addition, the enclosed microfossils that correlated with those found in the middle portion of the Karatau Series of the Urals [4] and so-called Ignikansk Association stromatolites in the Preduisk beds also supplies stratigraphic evidence for this statement. The stromatolites by themselves, or in combination with the other evidence provide correlation with the Katavsk interval that represents the beginning of the Upper Riphean-type [27] stromatolitic sequence.

The Kerpyl'sk Series, depending on different correlation criteria with the Ural stratotype, as articulated by different authors, is either placed into the top of the Middle, or the base of the Upper Riphean (discussion in the literature: [27, 32]). Established correlatives of the Kerpyl'sk Series; the Upper Sukhopitsk deposits of the Yenisei Ridge [25, 27, 32] include intrusions with U/Pb zircon ages of 990 Ma [5]. This value corresponds to the earlier published K/Ar ages of relatively high-K minerals of the glauconite group from the base of the Kerpyl'sk Series (1160-1020 Ma) [12]. Consequently, the Kerpyl'sk Series is older than 1000 Ma and can not be included into the Upper Riphean without a radical review of the isotopic age of the Middle/Upper Riphean boundary in the S. Ural type location. As for the Enninsk Formation of the Uchur Series, it includes the oldest dated minerals of all of our samples and, according to all indications, belongs to the Lower Riphean [25, 27, 32]. The age of the Lower-Middle Riphean boundary is 1350 ± 30 Ma [27].

TABLE 2. Mineralogical and Geochronological Isotope Data of Studied Samples

Sample No.	Index number of samples in publication [42]	Grain size, mm	Grain density, g/cm ³	Mineral composition	Sinterite layer ratio, %	b parameter, Å	K, %	⁴⁰ Ar _i , ng/g	Rb, µg/g	Sr, µg/g	⁸⁷ Sr/ ⁸⁶ Sr	Age*		Reference†
												K—Ar	Rb—Sr	
2	1	0,315—0,2	2,7—2,75	Gl	15—20	—	5,97	237	231	11,7	1,0972	496	458	1
3	2	0,315—0,2	2,7—2,75	Gl	15—20	9,09	6,14	212	238	13,2	1,0653	438	465	1
5	3	0,315—0,2	2,7—2,75	Gl	15—20	9,09	6,06	221	208	13,7	1,0136	460	472	1
E-98	4	0,2—0,1	2,7—2,75	Gl	10—15	9,08	6,00	218	186	27,4	0,8310	459	430	1
MM-11	5	0,2—0,1	2,7—2,75	Gl	10—15	—	5,93	—	197	20,1	0,8931	—	447	1
99/9	—	0,4—0,2	2,65—2,75	Gl	<5	9,10	7,24	263	187	15,2	0,9450	459	456	1
541	—	0,4—0,2	2,7—2,8	Gl	<5	9,06	6,96	263	198	16,7	0,9360	476	455	1
67/2G	10	0,4—0,2	2,55—2,63	Il	15—20	9,01	5,62	—	273	23,9	1,0542	—	707	1
563	11	0,1—0,063	—	Al—Gl	25—30	9,01	6,65	400	—	—	—	707	—	2
562	12	0,1—0,063	—	Il	15—20	0,02	6,27	440	—	—	—	802	—	2
561	13	0,1—0,063	—	Al—Gl	15—20	9,01	6,31	429	—	—	—	782	—	2
560	14	0,1—0,063	—	Al—Gl	15—20	9,01	6,39	432	—	—	—	779	—	2
558I	15	0,1—0,063	—	Al—Gl	15—20	9,01	6,73	456	—	—	—	779	—	2
555	16	0,1—0,063	—	Il	15—20	—	7,15	443	—	—	—	724	—	2
8a	17	0,1—0,063	2,7—2,75	Al—Gl	25—30	9,04	7,24	402	—	—	—	661	—	2
60	18	0,315—0,2	2,6—2,7	Il	10—15	9,02	7,40	490	291	23,2	1,1681	765	848	1
60/3	19	0,315—0,2	2,65—2,7	Il	<5	9,03	7,78	—	299	11,6	1,6682	—	820	1
24	20	0,1—0,063	2,6—2,7	Il	>30	9,04	4,56	236	—	—	—	624	—	2
49/1	—	0,16—0,1	2,5—2,65	Al—Gl	15—20	9,02	5,20	—	246	6,69	2,1347	—	822	1
40/10	—	0,2—0,16	2,45—2,5	Il	15—20	9,02	4,38	—	178	30,5	0,9168	—	844	1
43/4	21	0,63—0,315	2,6—2,65	Al—Gl	15—20	9,06	5,97	458	270	14,1	1,4441	861	864	1
314D	22	0,315—0,2	2,55—2,65	Al—Gl	15—20	9,03	5,98	—	282	15,3	1,4142	—	866	1
40/7	23	0,315—0,2	2,6—2,7	Al—Gl	15—20	9,06	5,87	—	313	13,3	1,6078	—	850	1
44/3	—	0,315—0,2	2,55—2,7	Al—Gl	15—20	9,04	4,45	—	195	26,2	0,9863	—	876	1
128	24	0,315—0,2	2,6—2,7	Al—Gl	15—20	9,05	6,53	—	295	20,8	1,2038	—	803	1
223I	25	0,16—0,1	2,65—2,75	Il	20—25	9,05	7,26	—	287	13,9	1,4159	—	774	1
19	—	0,4—0,2	2,65—2,75	Al—Gl	<5	9,06	7,49	800	—	—	—	1115	—	3
23	26	0,4—0,2	2,7—2,8	Al—Gl	<5	9,05	7,04	755	—	—	—	1120	—	3
85/5	27	0,4—0,315	2,75—2,8	Al—Gl	15—20	9,06	7,60	857	300	10,5	2,2679	1158	1140	1

*Some of the age values differ slightly from earlier published ones [8], due to additional analyses.

†Radiometric data obtained from: 1 — A. G. Rubleva (K/Ar); E. P. Kut'yavina; I. M. Gorokhova and others (Rb/Sr); 2 — S. B. Smelova [10, 15, and unpublished data]; 3 — M. M. Arakelyants [9].

Study Methods. Grains from the rocks are separated by the usual methods, including crushing or elutriation of the samples, sieving, scrubbing, drying at c. 30°C temperature, multiple cleansing of the largest grain size fractions by electromagnetic separator (SEM-1, SIM-1, etc.). Preferential treatment is employed for the relatively coarse fractions (> 0.2 mm), because of their easier separation but smaller fractions are often also utilized. Fractions are separated by the density method in special flasks and cylinders [13], ultrasound purification, a disperser (UZDN-2T) being used with distilled water. Separation of the magnetic concentrate in heavy liquids of 2.4-2.9 g/cm³ density at 0.02-0.05 g/cm³ intervals takes place by the use of calibrated density reference values (2.389, 2.4999, 2.6022, 2.6911 g/cm³). For further separation dominant density fractions are used, preferably the heaviest ones. The required values frequently were obtainable only for the lightest fractions.

Ultrasound grain preparation, depending on grain characteristics took anywhere from a few seconds to 15-20 min and involved the most weathered portion of the grains and overgrowths and also removed foreign matter from the fractures. Grains of glauconite (sample #541, Lower Cambrian) and illitic hydromuscovite (sample #60, Upper Riphean) have proven that moderate (5-30 min) ultrasound preparation does not affect mineral structures. Study of sample #60 has shown that during such preparation the K and Rb content and the calculated Rb/Sr age remained practically the same, and during preparation for less than 15 min the K/Ar age also remained the same (Table 1). This agrees with published data [47, 49] and shows that the preparation procedure was suited for grain preparation in age dating.

The separation procedure is completed by additional cleansing under binocular microscope. Following these procedures, the grains, available for mineralogical and isotope analysis, were at least 98-99% pure.

The mineralogical analysis is based on optical, chemical, diffractometric (x-ray and electron diffraction), infrared-spectroscopy, and Mössbauer methods that, with the exception of the last one, were conducted at respective laboratories of the Geological Institute, Academy of Sciences of the USSR. Mössbauer spectroscopy was performed at the IGGD of the Academy of Sciences of the USSR, with the use of electrodynamic assembly and constant-potential accelerator YaGRS-4, on the basis of multichannel analyzer LP-4840. The spectra were developed on a EVM BESM-6 with a program, formulated at the Institute of Electromechanics of the Academy of Sciences of the USSR [24], using the least squares method.

The K/Ar and Rb/Sr age determination method has been described [3, 19]. The accuracy of result was checked by comparison with All-Union Soviet and international standard samples. Feldspar sample #70 contained 524.5 µg/g Rb and 65.7 µg/g Sr, with a ⁸⁷Sr/⁸⁶Sr ratio of 1.2027. In SrCO₃ samples of Eimer and Amend the ⁸⁷Sr/⁸⁶Sr ratio was 0.7082 ± 7 (1 σ). In calculating the ages, the following constants were employed:

$$^{40}\text{K}: \lambda_e = 0.581 \cdot 10^{-10}; \lambda_\beta = 4.962 \cdot 10^{-11} \text{ yr};$$

$$^{87}\text{Rb}: \lambda = 1.42 \cdot 10^{-11} \text{ yr}.$$

The analytical error of K/Ar and Rb/Sr age determination was calculated as ± 3% (1 σ). Certain additional Rb/Sr age errors are caused by uncertainty in selecting the primary ⁸⁷Sr/⁸⁶Sr ratio in the minerals. This value in sea water may range between 0.7056-0.7096 [51] in the studied age interval. In the present work all Rb/Sr age models were calculated with the use of primary ⁸⁷Sr/⁸⁶Sr ratio 0.7090. Regardless of this largely arbitrary selection that introduces an error due to the high ⁸⁷Sr/⁸⁶Sr ratios the range of error in most samples apparently was not more than ± 1%. Isotope analyses had been conducted at VSEGEI (All-Union Geological Scientific Research Institute) for K/Ar ages and at IGGD of the Academy of Sciences of the USSR, for Rb/Sr ages.

Results. The study of authigenic globules was essentially conducted in terrigenous and terrigenous-clayey deposits. Only a few samples came from carbonate beds (samples #99/9 and 541) and weakly cemented argillites (sample #60). The structural-mineralogical analysis indicated that the Lower Cambrian glauconite-bearing rocks have undergone only initial epigenesis (katagenesis), while the Upper Proterozoic deposits have undergone deep epigenesis [8]. Mineralogical and isotope-age dating studies of the minerals are shown in Table 2.

Lower Cambrian of N. Estonia and the Aldan River Region. Samples from Estonian Lyukatsinsk Formation (Atdabansk Stage), exhibited significant "rejuvenation" both of the K/Ar- and Rb/Sr model ages (samples # 2, 3, 5, E-98, MM-11). The first two samples were dated

438-496 Ma, the others, 430-472 Ma. Based on the range of error, the values fell within the same range, although specific samples displayed different K/Ar and Rb/Sr ages. However, these differences overlap with the range of error. Mineralogically studied glauconite from these layers (three samples) have been reported as "rejuvenated" ones, although the somewhat greater K/Ar ages were between 504-537 Ma [30].

The Estonian samples in our collection consisted of glauconitic illite of the 1M polytype, with 10-20% smectite layers of relatively high K-content ($K_2O = 7.14-7.40\%$). The globules contained traces of Al-mica of polytype 1M (b parameter = 8.99 Å). The samples used in the work [30], mineralogically were close to ours, but contained a somewhat higher K content ($K_2O = 8.76-8.92\%$).

The study of Lower Cambrian (Tommotsk) glauconite globules of the Aldan River area (samples #99/9 and 541) also include admixtures (maximum 25%) of authigenic Al-micas of the 1M polytypes ($B = 8.97-8.98 \text{ Å}$) [8, 11]. These are glauconite samples, based on the K-content ($K_2O: 8.38-8.72\%$), the ratio of expandable layers (< 5%) and the structural perfection (polytype 1M). in agreement with a recommended criterion [45]. They represent an optimum variant for isotope dating and in this respect they are better than the Estonian glauconites. Nevertheless, their K/Ar and Rb/Sr ages are also significantly "rejuvenated" (K/Ar: 459-476 Ma; Rb/Sr: 455-456 Ma) and are close to ages of the Estonian samples. Among the earlier dated glauconite samples of the Tommotsk Stage from the middle course of the Aldan River, only four were mineralogically studied [22]. Their K/Ar ages ranged between 392-460 Ma and were close to those samples that we have investigated. Such similarity is remarkable, as samples, discussed in that publication [22] differ from ours in a lower K-content ($K_2O = 4.74-7.53\%$, as opposed to 8.38-8.72%) and in the large number of structural defects (polytype 1Md). In none of the Tommotsk glauconite sample groups did we find a connection between the K-content or the degree of structural perfection on one hand, and the calculated isotope age, on the other. All isotope age values went far beyond the acceptable value range for the corresponding time of deposition and early diagenesis of the enclosing sediments.

Upper Riphean of the Southern Ural. Minerals were dated from three levels of the Karatau Series: the Min'yarsk, Inzersk, and Zil'merdaksk Formations (Fig. 1).

In the Min'yarsk formation (#560-563) samples were selected from the thin (0.35 m) Zav'yalovsk unit in the area of the town of Min'yar. The K/Ar ages ranged between 707-802 Ma [10]. Considering the range of error, the range agrees with the one cited for ages of Upper Min'yarsk deposits (681-791 Ma [6, 29]), although the value range is certainly greater than given for the age range of deposition of the Zav'yalovsk unit. The dated mineral grains consisted of Al-glauconite and illite (sample #562) that have undergone certain deformation and slight chloritization. The minerals have good three-dimensional ordering (polytype 1M) and crystallographically are close to each other. The K-content is high ($K_2O = 7.55-8.01\%$). The ratios of expandable layer, displayed variations between different samples. In one sample (#563) the grains consisted of mixed-layer substances (25-30% smectite layers), in the rest (samples #560-562) they consisted of illite (15-20% smectite layer content). The K/Ar ages of illite (707-782 Ma) were lower than those of the mixed-layer mineral (802 Ma).

The illite samples from the upper part of the Inzersk Formation in the Min'yar city area are mineralogically similar to the Min'yarsk Formation illites (samples #560-562), based on their Al-glauconite (sample #558I) and illite (sample #555) content. Their K/Ar ages were 724 and 779 Ma [10]; the lower value is associated with a higher potassium content of the mineral (Table 2). These values are lower than earlier published ones for crystallochemically not investigated glauconite from the Inzersk Formation [29].

Globules, extracted from aleurolites of the Inzersk Formation at the Zilim River (sample #8a) and Al-glauconites of corresponding composition, have shown even lower (661 Ma) K/Ar ages. This is in agreement with the increased role of expandable layers (25-30%, but is unexpected because of the intrinsic higher K-content ($K_2O = 8.72\%$). In addition to the mentioned globular Al-glauconite-smectite an authigenic layers, micaceous minerals of the 2M₁ polytype (b = 9.00-9.03 Å)* also occurred in these aleurolites.

*Absence of crystallochemical data prevented exact identification of the layered minerals.

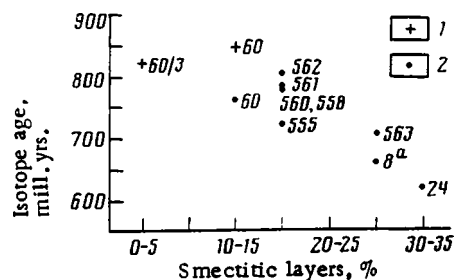


Fig. 3. Ratio of apparent isotope age and proportion of expandable layers in dated minerals of the Karatau Series of the Upper Riphean, S. Ural; 1) Rb/Sr age; 2) K/Ar age.

Two illitic samples have been analyzed from deposits, probably part of the Inzersk deposits near the town of Kisa†. Some of them are from argillites (#60), others from aleurolites (#60/3). The preservation of the grains was better in the argillites than in the aleurolites which thus contained deformed varieties and an authigenic, layered, micaceous mineral of polytype $2M_1$, with $b = 9.02 \text{ \AA}$ (sample #60/3). Better three-directional ordering (polytype $1M$) characterized the globules in these samples. The K-content ($K_2O = 8.91-9.37\%$) was high, the ratio of expandable layers varied little and was 10-15% in sample #60 and < 5% in sample #60/3. The model Rb/Sr ages of samples #60 and 60/3 were 855 and 820 Ma, respectively, while the K/Ar age of the first sample was 765 Ma. Differences between the K/Ar and Rb/Sr ages, the somewhat lower Rb/Sr values within the more altered rocks, and the agreement between the Rb/Sr values and the best known K/Ar age values in the glauconite-group minerals in other exposures of the Inzersk Formation [6, 29] were of interest.

The K/Ar age (sample #24) from the Zil'merdak Formation in the area of the town of Min'yar was 624 Ma, a strongly "rejuvenated" value. Illite-smectite globules of this sample have undergone various degrees of deformation and became slightly chloritized. Good three-dimensional ordering (polytype $1M$) characterized the mineral, distinctively low K-content ($K_2O = 5.49\%$) and significant (> 30%) proportion of expandable layers in the structure. In addition to the globular illite-smectite of type $1M$, authigenic, laminated mica minerals of polytype $2M_1$ also occurred in the enclosing rock. The b parameter was $9.00-9.03 \text{ \AA}$. Review of all age data from the Karatau Series indicate the following:

1) study of the samples, in comparison with many earlier data [6, 29], showed higher K-content ($K_2O = 5.50-9.37\%$, as opposed to $3.50-7.06\%$); (2) correlation between the K-content and calculated K/Ar ages was absent in all selected Karatau samples; (3) in all the selected samples and samples of individual formation, the correlation was negative between the expandable layer content and calculated K/Ar ages (Fig. 3); (4) the smallest age values of a given stratigraphic interval were associated with those beds in which laminated mica minerals of polytype $2M_1$ occurred, indicating greater rock alterations.

Riphean of the Uchur-Maisk Region. Eleven samples were analyzed from this region; from three widely separated stratigraphic horizons: the Upper Riphean Kandyksk Formation of the Uisk Series, the Middle Riphean Tottinsk Formation, Kerpyl'sk Series, and the Lower Riphean Enninsk Formation, Uchur Series (Fig. 2).

The Rb/Sr model age of sample #67/2G from the Kandyksk Formation at the Yudoma River was 707 Ma. The sample consisted of illitic hydromica of polytype $1M$. Strong color changes of the mineral caused a range of green-to-almost white coloration in the globules. Various, often very significant degrees of deformation were noted, along with low K-content ($K_2O = 6.77\%$, a 15-20% content of expandable layers, and traces of chlorite. This cast doubts on the stability of the geochemical isotope systems in this mineral. Nevertheless, its Rb/Sr age agreed with the K/Ar date (697 million years) of globular, layer silicate ("glauconite") earlier obtained from the same outcrop [12], but the isotope dates showed good agreement both with the age dates and the stratigraphic data, with regard to the formation's age and the unconformably overlying Vendian Yudomsk Series. A number of K/Ar ages had been published from this series, with a range of 580-623 Ma [12], but the clay fraction (< $1 \mu m$) of the basal horizon displayed a $639 \pm 20 \text{ Ma}$ Rb/Sr age, with a high ratio of primary $^{87}Sr/^{86}Sr: 0.7273$ [16].

†These deposits, in an isolated outcrop between deposit of the Zil'merdak Formation and the Lower Riphean beds, are believed to be Upper Riphean in age, based on their microfossil assemblages (identified by A. F. Veis), and belonging to the Inzersk Formation, based on lithological similarities.

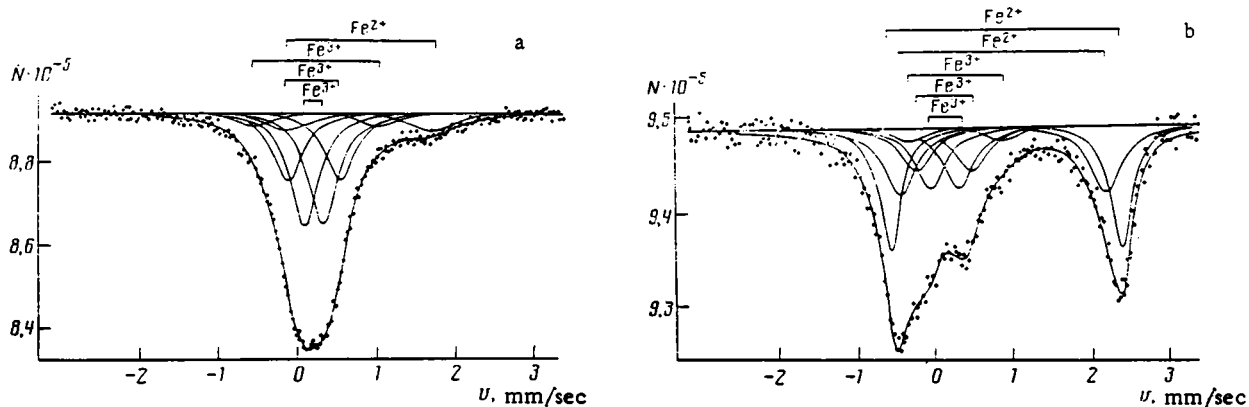


Fig. 4. Mössbauer spectra of studied samples. Hydromuscovite of illitic composition: a) sample #40/10; b) sample #60/3.

The most complete age data came from the Middle Riphean Tottinsk Formation in the Uchur-Maisk region. Contradictory data were derived from various parts of this very widespread formation.

Model Rb/Sr ages of the illitic (samples #40/10) and Al-glaucinitic hydromica (samples #49/1, 43/4, 314D, and 44/3) matter from the lower and middle portions of the formation along the Bol'shoi (Greater) Aim and Aim rivers ranged between 822-876 Ma. There was a certain decrease in the age upward in the section, although the range of age decrease was of the same order as the range of error. The K/Ar age of sample #43/4, 861 Ma, was in agreement with its Rb/Sr age (864 Ma). Illitic hydromuscovite displayed a high degree of crystallization (polytype 1M) and relatively low K-content ($K_2O = 5.27\%$), while the Al-glaucinite hydromuscovite, along with good three-dimensional ordering (samples #49/1 and 44/3) displayed certain structural disorders (polytype 1Md-1M), associated with a higher K-content ($K_2O = 7.07-7.20\%$). The proportion of expandable layers was uniform (15-20%); globule deformation did take place (sample #40/7 and 40/10), as did chloritization (sample #44/3) and calcitization (sample #314D).

Lower values of the model Rb/Sr age were obtained in samples from the lower part of the Tottinsk Formation in the Uchur River uplands (803 Ma; sample #128) and in the Kyllakhsk Ridge (774 Ma, sample #223I). These two samples, corresponding in composition to Al-glaucinite and illite, respectively, had high K-content ($K_2O = 7.87-8.75\%$), good three-dimensional ordering (polytype 1M) and 15-25% expandable layer content. Minor iron accumulation occurred as secondary change in sample #128 and chloride trace was found in #223I. The minimal ages of the Tottinsk Formation came from the fine fraction of sample #223I (Table 2). The mineral in this fraction displayed higher (20-25%) concentration of expandable layers and, as expected, with a high K-content ($K_2O = 8.75\%$). In contrast to other Tottinsk samples from horizontal Uchur-Maisk platform rocks this sample came from slightly deformed deposits, crushed by thrust-faulting in the marginal zone of the Yudomsk-Maisk Depression [27].

The isotope age of minerals that we have analyzed from natural outcrops of the Tottinsk deposits had significantly lower K/Ar Al-glaucinite-ages than probable correlative had in the Mokuisk stratigraphic test hole [9]. Between 2013-2141 m, dark aleurolitic-clayey beds contained microfossils. Lithologically the beds were close to the Tottinsk Formation, although several geologists correlated them with closer horizons of the section. Two Al-glaucinite samples from the 2013-2035-m interval displayed unique, 1115 and 1120 mill. yrs. K/Ar ages and similar mineralogical characteristics [8, 9]. They had good three-dimensional orderings (polytype 1M), high K-content ($K_2O = 8.48-9.02\%$), and had practically no expandable layers. There and in other Precambrian Ural and Siberian sections the globules were deformed and slight chloritization occurred. In this respect they do not significantly differ from other samples, discussed in that work, including those that have displayed evident "rejuvenation" of isotopic ages.

The K/Ar dates from the samples of the Mokuisk drillhole are comparable with earlier published [6, 12] K/Ar dates from crystallochemically not studied glauconite minerals from the Tottinsk ("Enninsk" and Omninsk) deposits. The samples displayed 1020-1136 Ma ages from the Middle Mai River Basin (70-140 km SE of our sample locations in the Greater Aim River

lowland (Fig. 2), and 1160 Ma for the sample from the lower course of the Greater Aim River.* These K/Ar dates agree with recent assumptions on the isotope age of the Tottinsk Formation, based on its stratigraphic position and correlation with like facies of the Yenisei Ridge, the minimum age range of which has been quite reliably established. At the same time, the ages of globular layer silicates from natural outcrops of the Tottinsk Formation were low, in comparison with assumed ages of the formation.

Only sample #85/5 was analyzed among the older horizons of the Uchur-Maisk Riphean sequence. The sample comes from the Lower Riphean Enninsk Formation, along the upper course of the Uchur River. Its K/Ar and model Rb/Sr ages were 1158 and 1140 Ma, respectively. The studied grains were deformed and, to a great extent replaced by goethite. The mineral was Al-glaucanite with high K-content ($K_2O = 9.16\%$), good three-dimensional ordering, but on the basis of expandable layers (15-20%) belonged to the hydromica category. The dates were significantly younger than the age of the Lower/Middle Riphean boundary (1350 ± 30 Ma) and comparable with the oldest K/Ar dates in the literature [8, 12] from geologically younger Tottinsk deposits that are separated from the Enninsk deposits by two regional unconformities and the time interval of deposition of the Aimchansk Series (Fig. 2).

Discussion. The obtained K/Ar and Rb/Sr dates formed the following time sequence, with upward decreasing age values: Lower Riphean 1140-1158, Middle Riphean 774-1120, Upper Riphean: 624-848, Lower Cambrian: 430-496 Ma. A significant part of the dates from the Lower Riphean Enninsk Formation, the Middle Riphean Tottinsk formation, the Upper Riphean Kandyksk Formation, the Lower Cambrian variegated and Lyukatisk Formation displayed a general agreement between the K/Ar and Rb/Sr ages. The dominant portion of these dates were, to varying degrees, younger than the stratigraphic ages of comparable formations.

Analysis of the crystallochemical characteristics of the dated minerals is of great interest, especially that of the K-content, the degree of structural ordering and the ratio of expandable layers. These are the features that are usually recommended for consideration in sample selection for isotope dating [45, 49]. Data on our samples and on those discussed in the literature from these horizons indicated no relationship between the K-content in the studied minerals of any of the units and the preservation degree of the K/Ar and Rb/Sr isotope systems. The K/Ar and Rb/Sr dates, in agreement with what was expected on the basis of stratigraphic data were obtained from minerals with relatively high (#19, 23, 60/3) or lower (#67/2G) K-content and from apparently "rejuvenated" samples (#99/9, 541, 223I and 85/5), with a K_2O content of 8.5-9%. Based on these examples, known also from the literature and following other workers [7, 20, 21, 26] we may conclude that the high K-content, typical of the pre-Mesozoic globular layered silicates, does not guarantee a reliable isotope age, reflecting the time of sedimentation or early diagenesis. Such a composition may only be regarded as a desirable characteristic of datable minerals, influencing the stability of their structure.

Data are still insufficient to judge the impact of various degrees of structural imperfections in minerals on the minerals being selected for age dating. Most mineral samples had a structural ordering of polytype 1M. Only three Al-glaucanite hydromica samples from the Tottinsk Formation displayed certain amount of structural disordering (polytype 1Md-1M). As the K/Ar and Rb/Sr ages of these samples agreed with ages of beds with structurally perfect Al-glaucanite and illite hydromicas, it may be said that such differences in the degree of mineral ordering — in case it was primary — do not involve differences in the stability of their isotope-dating system as far as "rejuvenation" processes are concerned. If one assumes that structural disorders accompany processes that cause "rejuvenation," one should acknowledge that destruction of the isotope system occurred at the same rate in all minerals, independently of their structural properties.

Expandable (smectitic) layers are likely locations for cation exchange, adsorbational and diffusional reactions that may lead to the destruction of isotope systems of layer silicates and for certain glauconite minerals have shown the correlation between the ratio of such layers and the cation-exchange ability [41, 45, etc.]. In one of our age-selected samples (Upper Riphean of the Ural), actually displayed a negative correlation between the ratio of smectitic layers and the calculated K/Ar and Rb/Sr ages (Fig. 3), also known from other examples [26, 39]. However no such correlation existed in other selected samples, reviewed

*Certain works [27], p. 68) erroneously give an Uchur River sample location.

in the present work (Lower Cambrian of Estonia and Siberia, Middle Riphean in Siberia) or described in [23, 43]. In one case an isotope age from the Kandyksk Formation agreed with the stratigraphic age of the enclosed mineral that contains 15-20% expandable layers, while minerals with but a minimal amount of such layers (less than 5%) may appear either as "rejuvenated" (Lower Cambrian units of the Aldan River area), or of reliable "true" ages (Tottinsk Formation in the Mokuisk drillhole). Thus, the influence of the smectitic component on the isotope ratios in the studied dioctahedral minerals cannot be interpreted simply. Incidentally, in contrast with a number of example in [20, 41, 45, etc.] in none of the studied samples was there a correlation between the K-content in the mineral and the ratio of its expandable layers, although these values have shown considerable variations in our samples (Table 2).

As in high-temperature micas (muscovite and biotite) and Al- and Mg/Fe-illite varieties [36], it might be expected that the isotope systems of illitic and Al-glaucanitic minerals are more stable, with respect to later influences than. (Fe-) glauconite, proper, is. However, the degree of isotope age distortion in various members of the isomorphous glauconite series was similar in the studied material (Al-glaucanite-illite and their structural varieties).

Thus, no correlations existed in the studied minerals between the calculated isotope ages and parameters, as the structural ordering, the ratio of expandable, and the concentration of individual chemical components. Within specific examples, regular variations of apparent ages did occur in relation to these parameters (but in each such instance, only a single parameter varied). Apparently, the search for ties between the behavior of the isotope-age dating system and the crystallochemical characteristics must proceed on more sophisticated levels of research.

In conjunction with these considerations, we must review certain characteristics of the Mössbauer spectra of the studied minerals. The spectra represent the superposition of quadrupole doublets of the Fe^{2+} and Fe^{3+} ions. Three doublets occurred in Fe^{3+} ions. The most intensive of these were the quadrupole separation of $\Delta \approx 0.3$ mm/sec, and isomeric shift (relative to Na-nitroprusside) of $\delta \approx 0.20$ mm/sec, apparently correspond to the Fe^{3+} ion in octahedral configuration, located in the most uniform charge field. A less intensive doublet, characterized by $\Delta \approx 0.77$ mm/sec and $\delta \approx 0.20$ mm/sec is a superimposed doublet of the Fe^{3+} ions in the octahedral layer in a less uniform charge setting and of Fe^{3+} ions, adjacent to Al that replaces Si in the tetrahedral layer through isomorphous substitution. The least intensive doublet of $\Delta \approx 1$ mm/sec and $\delta \approx 0.27$ mm/sec is attributed to the Fe^{3+} ion in a field with an (OH)-anion deficit.

Very low-intensity absorption lines characterized Fe^{2+} in spectra of most of the studied samples (#2, 3, 5, E-98, 99/9, 541, 40/10, 43/4, 314D, 128, and 85/5). The positions of the lines sometimes can not be clearly determined due to the very diffuse absorption signal of the 1-2 mm/sec zone and the described lines with exclusively great half-width (~ 0.80 mm/sec). A typical spectrum of this category is shown in Fig. 4a, and this signal is attributed to the charge transfer between the Fe^{3+} - Fe^{2+} ion pairs [42]. In this case the iron acquires something like an intermediate valence with Mössbauer parameters that intermediate between the parameters of ions Fe^{3+} and Fe^{2+} . It is important that information on the existence of the Fe^{3+} - Fe^{2+} charge exchange be obtained only when the octahedral layer holds nonisolated Fe^{3+} - Fe^{2+} ion pairs and their series, or even an entire field such occurrence [34]. It follows, that most studied minerals in the octahedral layers apparently contain fields enriched in iron ions.

The cited signal, with a shoulderlike configuration, was absent in the studied material only in spectra of samples #60 and 60/3 (Inzersk Formation, S. Ural). In these minerals of low iron content, an isomeric shift and quadrupole separation of the Fe^{2+} ions was clearly determined. Two Fe^{2+} ions was clearly determined. Two Fe^{2+} ion doublets were identified. These usually are attributed to trans(M1)- and cis(M2)-positions in the octahedral lattice of the mineral (Fig. 4b). The absence of the "shoulder" apparently is caused by the even iron distribution in the octahedral layer and the absence of chains or fields of the Fe^{3+} - Fe^{2+} ion pair.

Of all the samples for which Mössbauer spectra were obtained, only samples #60 and 60/3 displayed Rb/Sr isotope ages that were close to assumed ones, based on stratigraphic data;* although the K/Ar age of one of the samples showed slight "rejuvenation".

Minerals that contained evenly distributed iron in the octahedral layer probably had a more stable structure in resisting secondary alterations, in contrast with minerals in the octahedral layers that contained fields with high iron-cation concentrations. Of course, a larger body of data is required in deciding the question in a satisfactory way. Mössbauer spectra have already been recommended in the solution of diagnostic problems of secondary glauconite mineral alterations [1, 18, etc.]. However, the cited works used different approaches and diagnostic characteristics.

Turning from the crystallochemical field of research, we attempt now to analyze the geological factors that may have been responsible for the destruction of the isotope systems in the studied minerals. Almost all of our samples, dated by both the K/Ar and Rb/Sr methods displayed similar isotope ages. The problem is the following: does an agreement between the Rb/Sr and K/Ar ages of these minerals help to date certain specific geological events, and if so, which ones?

Comparative studies of the behavior of the Rb/Sr and K/Ar systems in glauconite under the impact of natural processes have been rather scarce. Their analysis indicates that weathering leads to an age ratio of $(K/Ar) > t(Rb/Sr)$, as the heat effects in the zone of katagenesis and anchimetamorphism produce a reverse pattern [45, 49, 50]. It is also assumed that the geological events that include circulation of a liquid phase, may lead to the total loss of radiometric products from glauconite and to an agreement between the apparent Rb/Sr and K/Ar ages [38].

There are geological explanations for the destruction of the geochronological isotope systems in glauconitic minerals. The main explanation for changes in the K/Ar ages involve the heating of beds during "burial metamorphism" (epigenesis and anchimetamorphism). The basis of this premise involves assumptions in the literature about low-temperature diffusion of ^{40}Ar from glauconite [37] and experimental data on the start of loss of radiogenic ^{40}Ar from the mineral structure at temperatures of 200-250°C [20, 26, 45]. Such a ^{40}Ar loss possibly is associated with the rejuvenation of individual samples from the Upper Riphean deposits of the Ural near the town of Min'yar and the Zilim River (Table 2). Such an assumption is in agreement with findings in the Inzersk samples, with ratios of $t(K/Ar) < t(Rb/Sr)$ and the presence in the Zil'merdansk and one of the Inzersk samples of laminated, micaceous minerals of polytype $2M_1$, indicative of more intensive rock alteration.

Such an explanation is not applicable in the other studied regions. Lower Cambrian deposits in Estonia and along the Aldan River, with significantly "rejuvenated" glauconitic dates were nowhere buried at depths of more than 1 km. Riphean beds of the Uchur-Maisk Platform, also displayed a large number of "rejuvenated" dates in the investigated silicates, although the lowest horizons were buried at depths of 2-2.5 km. They produced positive correlation between the isotope ages and the stratigraphic ones. All these layers displayed good agreement between the K/Ar and Rb/Sr dates. The "rejuvenation" may not be attributed to tectonic deformation effects; all Estonian, Aldan and, with the exception of sample #233I, Uchur-Maisk samples were taken from horizontally bedded deposits.

Nikolaeva thought that "rejuvenation" of K/Ar isotope systems in glauconite-group minerals was controlled by chemical and structural mineral changes, associated with processes of ancient (continental and mostly, underwater) weathering and that the trend of alterations was significantly influenced by primary facies zonation of the chemical composition of these minerals and the enclosing sediments. The intensity of chronological relationships of the glauconite-bearing beds and the periods of the main fold deformation [20 and 21] also played major roles in this theory. The application of this model to the objectives at hand create great problems. In our examples, rejuvenation processes occurred equally within various sediment facies. The three structural-isotope series were equally represented among the minerals and led to agreement between the K/Ar and Rb/Sr dates. Studies of contemporary profiles [45, 49, 50] have indicated at the same time that during weathering the K/Ar age of glauconite becomes greater than the Rb/Sr age.

*After this paper was sent to the printer, similar Mössbauer spectra were also obtained from samples #67/2G (Upper Riphean, Kandyksk Formation) and 23 (Tottinsk Formation, Middle Riphean). The isotope dates agreed with stratigraphically expected ages.

Change in the radioactive dates of minerals may be caused by regressive epigenetic processes (katagenesis), formed particularly by the tectonic uplift of a region and introduction of glauconite-bearing beds into the zone of meteoric waters [20, 40, 44]. The strongest such connection was demonstrated by Morton and Long [44]. They established that the Rb/Sr isochrons in glauconite of Texas Paleozoic deposits dated unconformities that separated glauconitic beds from overlying units.

The analysis of our material similarly suggests that "rejuvenated" K/Ar and Rb/Sr dates in a number of instances coincided with established or assumed isotope ages of stratigraphic unconformities in regional sedimentary sequences. The K/Ar and Rb/Sr ages of the early Riphean Enninsk Formation (1140-1158 Ma) agree closely with the age of the regional unconformity and reorganization of the Uchur-Maisk platform structure. These have preceded the Kerpyl'sk Series (~1200 Ma; [27]). K/Ar and Rb/Sr-ages of Tottinsk Formation samples from the Greater Aim River region (822-876 Ma), essentially overlapped with assumed ages of the lower boundary of the Uisk Series (800-850 Ma). The base of the westernmost outcrops of the series, geographically nearest to the Greater Aim Basin (Fig. 2), shows traces of erosion, indicating the importance of source area uplift W and E of the present position of this Series [27]. The K/Ar and Rb/Sr-ages (393-477 and 455-456 Ma, respectively) of Lower Cambrian glauconites in the Aldan River area [22], essentially agree with the age of the Middle and Late Ordovician, an early stage in the existence of the continental unconformity, as the prolonged interruption in sedimentation started in the part of Siberia in the Late Cambrian, lasting into the early Mesozoic.

Estonian data are highly important in this respect. The cited K/Ar and Rb/Sr dates of glauconite minerals from the Lower Cambrian (Atdabansk) Lyukatisk Formation (438-496 Ma and 430-472 Ma, respectively) coincide within the error range with the K/Ar glauconite dates of geologically much younger phosphorite deposits in the Pakerortsk Horizon (Rakvere, Estonia, and Kingisepp, Leningrad District). This age range is 458-490 Ma. The K-content of the samples in question was 5.72-6.45% (based on six samples, collected by G. P. Dubar, analyzed at VSEGEI). The conodonts and acritarchs dated the Pakerortsk Horizon as Upper Cambrian (Upper Franconian)-Tremadocian (Ordovician; [2]). The phosphoritic layers occur in the lower part of the Horizon. The isotope age of the Cambrian/Ordovician boundary currently is calculated at either 505 [31] or 495^{+5}_{-10} Ma [45]. If this age range is correct, the K/Ar dates of the Pakerortsk glauconites reflect a certain amount of rejuvenation.

The overlapping "rejuvenated" isotope ages of varied geological units (Lyukatisk Formation and Pakerortsk Horizon) mark the end of the early/beginning of Middle Ordovician. A laterally persistent Late Argenig unconformity occurs in the stratigraphic interval of N. Estonia. Its isotope age is apparently close to 470-480 Ma, the age of Lower/Upper Arenig boundary, currently calculated as 475^{+10}_{-5} and 470 ± 10 [45], or 478 and 488 Ma [31], respectively. The clustering of "rejuvenated" Lyukatisk and Pakerortsk glauconite dates around the isotope age of the Late Aregin unconformity is hardly accidental. Effects of regressive epigenesis, concurrent with the existence of the exposed unconformity surface probably were also responsible for the destruction of the geochronological isotope system of glauconites in the Lyukatisk and Pakerortsk deposits.

While it is attractive, the model is unsatisfactory. The isotope systems of the investigated minerals reacted in certain ways in being exposed to a given unconformity, but remained unaffected by other, younger and older unconformities. The answer to these problems posed requires still more data from additional materials of geochronological isotope systems and more detailed analyses of regional geological data. The following assumptions seem to be appropriate: (1) reorganized geochronological isotope systems of the studied material that was used in dating were linked only with those uplifts that resulted in abrupt changes in the regime and/or chemistry of pore waters, due to introduction of glauconitic beds to relatively high altitudes; (2) the isotope systems, reconstituted during a break in sedimentation apparently have lost their ability to reorganize during the next depositional break. If the first of these assumptions is correct, a useful tool may become available for geologists, not only for age dating, but also for establishing age ranges of certain unconformities.

* * *

The data that we have obtained and gleaned from the literature indicate that globular dioctahedral 2:1 layer silicates; glauconite, Al-glauconite, illite and their structural

varieties were able to form closed system with respect to K, Rb, Ar, and Sr-isotope since a certain point of time in geological history. These isotope systems become closed systems in the mineral during sediment accumulation (early diagenesis) at the earliest. Frequently, this occurs later. The length of this time interval prior to the closing of the system, entirely depends on various aspects of local geological history and varies from one location to another within a wide range. Statements on the exact or most likely magnitude of isotope age "rejuvenation" (10-20%) in the studied minerals are but unjustified simplifications. A single model can not explain the behavior of the Rb/Sr and K/Ar systems in the dated minerals. In each specific case one must search separately for reason (s) for the closing and destruction of such isotope systems.

Dating procedures that, especially in the domestic literature, until recently used individual glauconite samples and relied on results of interregional correlations, do not promise future improvement in dating stratigraphic units. Detailed studies that do include mineralogical studies of minerals to be used in dating, the parallel use of the K/Ar and Rb/Sr methods, determination of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and analysis of all stratigraphic, geologic and lithologic data that relate to the formation history and rock alteration must be employed in correlating isotope age data with specific events of geological history in a given region.

Until we are able to judge a priori whether a given sample could be helpful in reflecting past specific events in sedimentary rock evolution, globular 2:1 layer silicates apparently may not be prime means in long-distance correlation and geochronological time scale calibration. Isotope dates of boundaries in present stratigraphic time scales, based solely on K/Ar dates of such minerals should be thoroughly reexamined; possibly totally overhauled.

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New data are reported on the geology, mineralogy, geochemistry, and genesis of alunite-bearing metasomatites from the Began deposit. Two sets of altered rocks are identified, and the principal mineral parageneses are described; the mechanism is suggested for the formation of the metasomatites, specifying the distribution patterns of the principal and accessory elements in the deposits. The formation scheme of the deposit is reconstructed. The practical applications of the research for exploration, reconnaissance, and mining of similar deposits are described.

Due to its limited erosion, good preservation, a relatively simple geological structure, and a large amount of geological exploration data available, the Began deposit is a convenient object for studying the alunite deposits of volcanic type as such and, in general, the subsurface metasomatic formations in areas of postvolcanic activity. Numerous investigations of this deposit [6, 7, 15, 16, 18-23, 27, 30, 32, 35, 36, and other publications] provide extensive information on the geology, formations, and genesis of this area. In the present paper we offer some new data on the geological structure and mineralogic-geochemical features of alunite-containing metasomatites, shedding new light on their formation conditions.

GEOLOGICAL STRUCTURE

The Began deposit, situated 12 km northwest of Beregovo in the Transcarpathian region, in geotectonic terms is part of the Intracarpathian Middle Massif. It lies in the horst zone of the conjugation of Transcarpathian inner trough with the Greater Hungarian depression and is confined to the Subpannonian deep fault located in this area. The deposit was formed during the early orogenic stage of Alpine tectogenesis and is associated with processes of reflected activation that affected the Intracarpathian Middle Massif, where one of its manifestations was block movement in the horst zone of the Subpannonian fault and active volcanic and postvolcanic activity [19, 38].

The Began ore field consists mainly of volcanogenic and sedimentary Neogene rocks occurring on a Mesozoic basement of the horst zone. The deposit lies amid beds of the Lower Sarmatian liparitic tuffs of the Dorobratov suite, separated into horizons by two argillite interlayers [23]. Structurally, the Began deposit is a gentle anticline divided by faults into blocks [32]. The deposit consists of two sections: the Began area and the Dedovsk area, located 1 km from one another (Fig. 1). In the Began section the principal downthrow fault (the Maisk zone) and the surrounding plumage of cracks contain a barite-polymetallic mineralization; in the Dedovsk area these cracks are devoid of ore.

In either section the set of metasomatic rocks in altered liparite tuffs is largely the same: monoquartzite, alunitic quartzite, argillite, adularisite, and propylite; there is also a developed opalization zone and the so-called oxidation zone, identified by the presence of iron in an oxide form. The spatial correlations of these units determine the geological structure of altered rock massifs.

Alunite quartzites form in each section thick lens-shaped or bed-shaped bodies, stretching and gently dipping from the main fault disruptions in a northeasterly direction. Argillite, adularized rocks, and propylites progressively envelop alunitic quartzite from below, from the sides, and sometimes from the top. The presence of a zone of argillites in roof of lunitic quartzites, succeeded closer to the surface by a zone of adularized rocks, has

All-Union Scientific-Research Institute of Aluminum, Magnesium, and Electrode Industry, Leningrad. Translated from *Litologiya i Poleznye Iskopaemye*, No. 5, pp. 97-111, September-October, 1987. Original article submitted July 23, 1985.

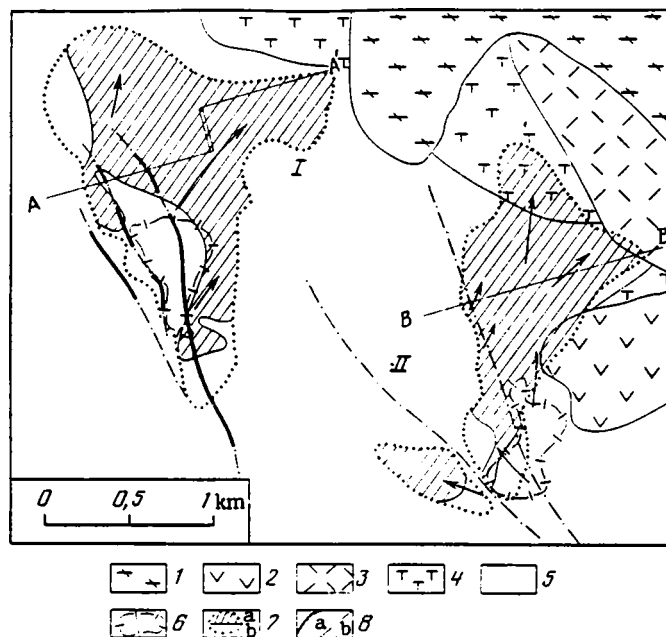


Fig. 1. Schematic geological map of the Began deposit (based on the data of Yu. V. Sabov): (1) clay, sand, tuffite ($N_{1-2}kb$); (2) andesitic basalt ($N_{1-2}pn$); (3) clay, tuffosandstone, etc. (N_{1al}); (4) siltstone, tuffite, etc. (N_{1lk}); (5) liparitic tuff (N_{1dr}); (6-7) areas of metasomatites developed after liparitic tuffs, (6) monoquartzite, (7) alunitic quartzite (a-opalized; b-without opal); (8) disruptive faults (a - enclosing barite-polymetallic ores; b - no ore); AA' and BB' are lines of sections shown in Figs. 2 and 3; (I, II) areas (I - Began; II - Dedovsk).

been established in the northern part of the Began area and in the northeastern and southern parts of the Dedovsk area. In the northeastern part of the Began area two horizons of alunite quartzites have been described, separated by zones of argillized and adularized rocks (Figs. 2 and 3). Alunitic quartzite, argillisites, adularized rocks, and propylites thus form a series of conformably occurring metasomatic bodies. The sereis constitutes a common metasomatic column traceable from the center in various directions, including the direction up the section, and in the opposite directions between the two horizons of alunitized rocks.

The boundary between pyrite- and hematite-bearing rocks, generally occurring in the near-surface horizons, has a complex occurrence pattern, largely determined by the geological structure of the deposit. The boundary is traced at a minimal depth (50 m) in the zone of principal downthrow faults of the Began area and, at a distance, subsides noticeably (up to 100-180 m). In both areas the boundary between pyrite and hematite rocks is largely conformable to the contour of alunitic quartzites. Where isolated alunite bodies appear at different depths, the boundary may have a zigzag shape in section (see Fig. 2). This pattern of the hematite rock boundary suggests that these rocks were formed simultaneously with the metasomatic alunitization column and with participation of the same endogenous and exogenous factors. No formations caused entirely by exogenous processes are observed in the alunitic quartzites.

Monoquartzite and opalized rocks occur near the surface: the former, near disruption faults; the latter, at some distance from them. Monoquartzites are found usually amid alunitic quartzite, but are often in contact with argillisites, i.e., show a disconformity with respect to the zones of the metasomatic column. The disconformities are even more pronounced in the opalization zone. It is confined to the subsurface horizons and crosses the boundaries of all metasomatites (except for monoquartzites). The disconformable occurrence of the opalization zone has been established in all the sections studied. Disconformities are particularly distinct at the flanks of the deposit, where the metasomatite boundaries have a high angle

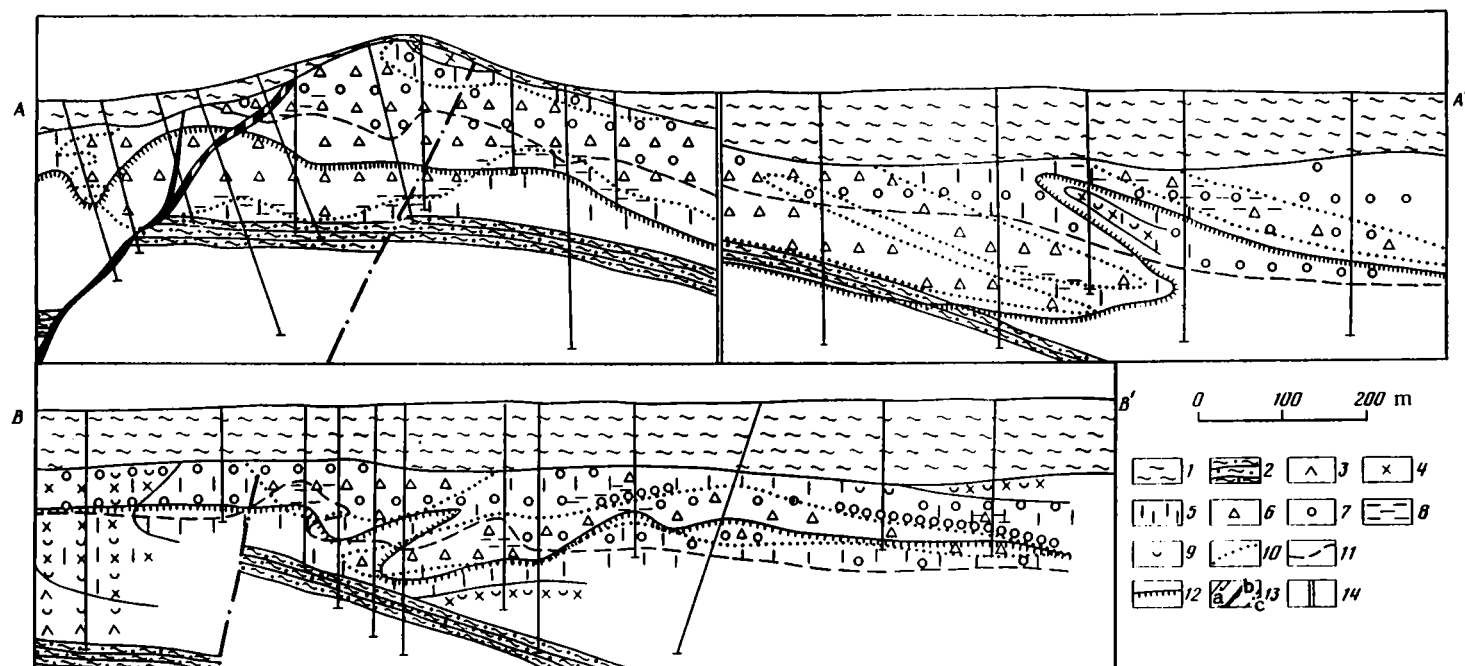


Fig. 2. Distribution of the mineral parageneses of metasomatic rocks on sections along the AA' and BB' (see Fig. 1): (1) Quaternary sediments; (2) upper sedimentary bed of the Dorobratov suite (Lower Sarmatian); (3-9) mineral parageneses [(3) albite-calcite-quartz with chlorite?, (4) adularia-calcite-quartz, (5) kaolinite-dickite-quartz, (6) alunite-quartz, (7) opal (condensations of marks indicate the areas of monoopalites), (8) halloysite, (9) montmorillonite-hydromicaceous mineralization]; (10) 20% contour of alunite deposit; (11-12) boundaries [(11) opalization zone, (12) between hematite and pyrite rocks]; (13) disruptive discontinuities [(a) with baritic mineralization, (b) with polymetallic mineralization, (c) ore-free]; (14) section transfer line (see Fig. 1).

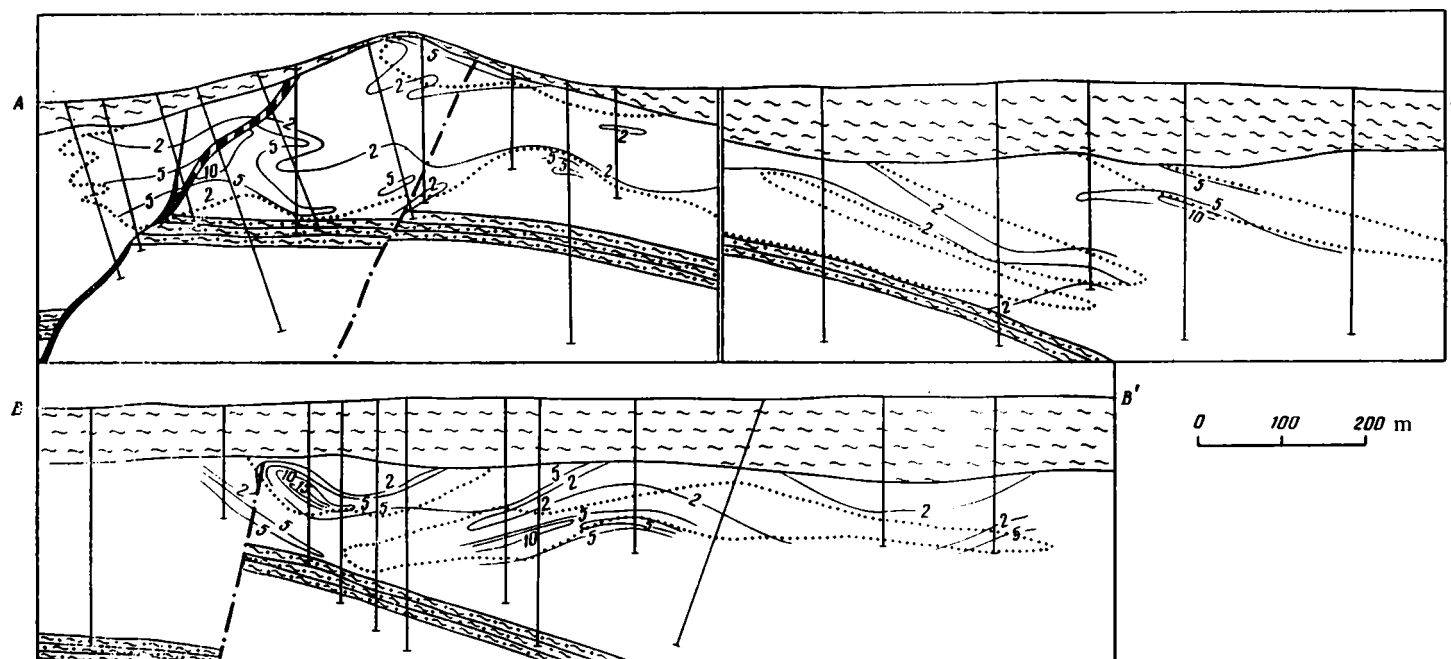


Fig. 3. Iron contents (in the form of Fe_2O_3 , wt.%) in metasomatic rocks on sections along the lines AA' and BB' (see Fig. 1). Notations as in Fig. 2.

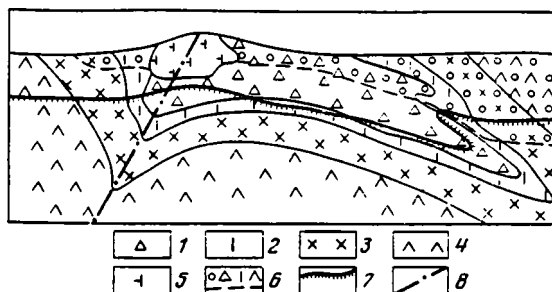


Fig. 4. Spatial interrelationships of metasomatic rocks in the section of the Began deposit: (1) alunitic quartzite; (2) argillizite; (3) adularized rocks; (4) propylites; (5) monoquartzites; (6) opalization zone; (7) boundary between hematite and pyrite rocks; (8) disruptive discontinuities.

in the subsurface zone. The location of the opalization zone is affected by the situation of the metasomatites of the alunite-propylite series (see Fig. 2). Alunitic quartzites do not favor the development of an opalization zone, whereas in argillizites and adularized rocks its thickness is noticeably increased. In that respect, the occurrence of monoopalites is also typical (these are the most intensely opalized rocks, containing up to 95% opal); beds of these rocks occur in argillizites directly under the roof of alunite deposits (see Fig. 2).

Two sets of metasomatic rocks can be identified in the Began deposit: (1) alunitic quartzites, argillizites, adularized rocks, and propylized rocks occurring conformably and constituting a common metasomatic column traceable in each section from the principal faults in various directions; and (2) opalized rocks and monoquartzites occurring with a discontinuity in relation to the metasomatites of the first set (Fig. 4).

MINERAL COMPOSITION AND PARAGENESES OF METASOMATIC ROCKS

The mineralogy of metasomatic rocks of the Began deposit has been described in [2, 3, 23] and other publications and is not discussed here at length. The mineral composition is the main criterion in defining the varieties of metasomatic rocks; it includes both common (ubiquitous) minerals and those minerals that are specific for each particular rock. Widespread in all the metasomatites are pyrite, hematite, and especially quartz, occurring as relict crystalloclasts and as neomorphous allotriomorphic-granular aggregates (microquartz).

Propylitized rocks consist of albite, quartz, montmorillonite, hydromica, carbonate, chlorite, and pyrite. One can only speak hypothetically about the paragenesis of propylites, because these rocks have been studied little and contain large quantities of microgranular poorly crystallized phases. The main mineral paragenesis includes albite, calcite, quartz, and some pyrite and chlorite.

Adularized rocks are identified by the presence of adularia in amygdaloids; chlorite is not typical. Their mineralogical composition is otherwise similar to that of propylites. Adularized rocks of the Dedovsk area are different from similar rocks of the Began area in a heightened content of montmorillonite and a lowered content of hydromica. The main mineral paragenesis of adularized rocks includes adularia, calcite, microquartz, and pyrite (or hematite). In the transition zone between adularized rocks and propylites, substitution of albite for adularia is observed distinctly, i.e., the development of adularized rocks from propylites.

Argillized rocks consist mainly of kaolinite (dickite) and quartz, with a subordinate amount of montmorillonite, hydromica, pyrite, hematite, and barite. X-ray diffraction and infrared spectroscopic studies of the principal clay mineral of these rocks, previously assumed to be kaolinite, showed that it is a mix of kaolinite and dickite, with dickite being predominant in the Began area and kaolinite in the Dedovsk area. The main mineral paragenesis of argillized rocks is (dickite)-quartzose kaolinite with pyrite and hematite. Barite is commonly found in argillized rocks, especially in the Began area. Barite is al-

TABLE 1. Contents of Principal Chemical Components and Minerals in Alunitic Quartzites, Began Deposit

Component	Began area				Dedovsk area				Mean for deposit
	I	II	III	mean for area	I	II	III	mean for area	
SiO ₂	58.53	56.38	58.25	57.33	56.99	49.50	36.34	52.47	55.77
Al ₂ O ₃	14.54	14.98	13.34	14.60	15.66	18.11	20.20	17.04	15.38
SO ₃	12.26	13.87	17.30	13.89	13.34	15.94	30.74	15.31	14.34
BaO	0.67	0.60	0.58	0.62	0.23	0.11	0.19	0.17	0.48
K ₂ O	3.55	3.83	3.50	3.63	3.38	4.03	4.12	3.73	3.66
Na ₂ O	0.09	0.11	0.10	0.10	0.43	0.26	0.28	0.34	0.18
TiO ₂	0.80	0.78	0.80	0.79	0.53	0.30	0.24	0.41	0.67
Fe ₂ O ₃	0.26	2.08	3.48	1.73	2.15	3.14	9.17	2.92	2.11
P ₂ O ₅	0.13	0.08	0.07	0.09	0.13	0.12	0.14	0.13	0.10
CaO	0.10	0.08	0.04	0.08	0.10	0.28	0.30	0.20	0.12
MgO	0.03	0.06	0.05	0.05	0.05	0.15	0.11	0.10	0.06
SO ₃ (a.s.)	10.67	13.30	12.82	12.41	11.51	15.86	16.74	13.95	12.90
SiO ₂ (a.s.)	19.33	1.53	1.24	7.00	31.02	3.02	3.07	16.18	9.94
Alunite	30.6	35.7	33.5	33.8	32.5	41.6	43.8	37.4	34.9
Opal	19.7	Traces	Traces	6.1	31.6	Traces	Traces	14.8	8.9
Quartz	38.0	55.3	58.0	50.3	23.1	47.0	32.2	35.2	45.5
Metahalloysite	10.4	5.9	3.0	6.9	10.2	8.0	11.3	9.2	7.6
Hematite	0.3	2.1	1.4	1.4	2.2	3.2	0.8	2.6	1.8
Pyrite	Traces	Traces	3.2	0.5	Traces	Traces	11.6	0.5	0.5
Barite	1.0	1.0	0.9	1.0	0.4	0.2	0.3	0.3	0.8
Kaolinite (dickite)	Traces	Traces	Traces	Traces	Traces	Traces	Traces	Traces	Traces
Magnetite	»	»	»	»	»	»	»	»	»
Goethite	s.g.	»	None	»	»	»	None	»	»

Note. (I-III) types (I - opal-alunite, (II) quartzalunite, (III) pyrite-bearing quartz-alunite); a.s. = alkaline-soluble; s.g. = single grains.

ways corroded by kaolinite (dickite), hematite, and microquartz of the groundmass. Argillized rocks were therefore formed largely after barite. In the transitional zone between argillized and adularized rocks, which is up to 100 m thick, adularia, calcite, montmorillonite, and hydromica are sometimes replaced by kaolinite (dickite), sometimes forming a kaolinitic (dickite)-quartzose rock, i.e., an argillite zone grows at the expense of adularized rocks.

Alunitic quartzites consist of two principal minerals: alunite and quartz. Minor quantities of halloysite, pyrite, hematite, and barite are present. In subordinate amounts kaolinite (dickite), magnetite, goethite, and other minerals are found; no chalcedony has been established. Large quantities of opal are contained in the opalization zone of alunitic quartzites. Three types of alunite rocks are distinguished by their mineral compositions: opal-alunitic, quartz-alunitic, and pyrite-bearing quartz-alunitic. The average chemical and mineral compositions of each type are given in Table 1.

Alunite is found in amygdaloids, the groundmass, and small veinlets. In amygdaloids it appears as an aggregate of large idiomorphous crystals, but more often as small grains recrystallizing into small crystals. In the groundmass, alunitic grains have an irregular angular form and are closely intergrown with microquartz. Small alunitic grains in the groundmass often appear as separate relicts with simultaneous extinction. Microquartz of the rock near such grains becomes noticeably larger in some of the schlieren veinlets and small zones cutting across alunite; alunite crystals in amygdaloids are not corroded and retain their idiomorphous outline. This seems to indicate a redistribution of alunite inside the micro-quartz-alunitic rock: it is extruded from the groundmass and redeposited in amygdaloids. Some of the alunite component may be washed out, but there is no noticeably depletion of the rock in alunite.

The alunitic veinlets may be either pure alunite or contain also barite, sphalerite, and pyrite, in an equilibrium coalescence with alunite. Generally, in secondary deposits, however, barite is corroded by alunite. Alunite in barite-sphaleritic veinlets has a different morphology, chemical composition, and physicochemical properties than alunite in the true alunitic veinlets and the general alunite in the deposit (Table 2). Probably, it is an earlier generation of the mineral.

Barite is widespread in alunitic quartzite of the Began deposit. It is found mainly in principal faults of the Began area and the surrounding cracks. Substitution of alunite,

TABLE 2. Chemical Composition of Alunite from Veinlets in the Began Area, %

Component	True alunite veinlets		Alunite veinlets with barite and sulfides	
	hole 735, depth 114.0 m	hole 734, depth 58.0 m	hole 726, depth 125.5 m	hole 724, depth 181.0 m
SiO ₂	Not det.	Not det.	0.28	0.21
Al ₂ O ₃	36.32	37.24	36.30	36.31
Fe ₂ O ₃	0.27	0.06	0.10	0.15
SO ₃	37.50	38.09	37.24	37.80
BaO	0.67	0.53	0.47	0.49
Na ₂ O	0.08	0.17	0.29	0.64
K ₂ O	9.68	9.40	10.10	9.80
H ₂ O	13.40	13.44	13.05	13.50
K ₂ O/Na ₂ O	116.3	53.2	36.3	15.3
Deficit of alkaline metals, rel. %	10.3	13.2	3.1	2.5

microquartz, opal, and halloysite for barite is frequent. The rock alunitization is somewhat delayed compared with baritic mineralization.

Metahalloysite is found almost everywhere in alunitic quartzites. Usually, it cements alunite crystals in amygdaloids without any trace of corrosion, although in late metahalloysite veinlets and in areas of intense halloysitization it replaces alunite.

Barite-alunitic paragenesis with sphalerite and pyrite is the most prominent paragenesis of alunitic quartzites. The alunite-quartz paragenesis (with hematite or pyrite) is the main paragenesis of the rock; barite is unstable with respect to it. At a later stage metahalloysite occurs next to alunite and quartz; in the final periods of evolution it corrodes alunite and microquartzite, giving rise to a metahalloysitic paragenesis with pyrite, hematite, or goethite.

At the boundary between alunitic quartzite and kaolinite-dickite rocks an alunite-quartz paragenesis is observed, which is formed at the expense of kaolinite (dickite)-quartz paragenesis; alunitic quartzites are thus formed at the expense of argillites, which are external with respect to them.

An opalization zone is observed in the top horizons throughout the deposit, which develops on all metasomatites (except for monoquartzites). The superimposed nature of the opalization with respect to the leading rock paragenesis is always obvious. In particular, opal develops in alunitic quartzite in the groundmass and the amygdaloids. The degree of opalization of the groundmass varies from mild to almost complete. In the groundmass of an opalized rock the structural features of mature microquartz rock can be observed: aggregated microquartz grains and alunite grains corroded by them. In amygdaloids the simple cementing of alunite crystals by opal is associated almost everywhere with a corrosion of alunite by opal. Traces of subsequent dissolution - cavities and voids often filled with metahalloysite - are often seen in opal. In the initial opalization periods an opal-alunite paragenesis thus exists in alunitic quartzite which later gives way to opal paragenesis with hematite or pyrite. Metahalloysite develops after opal.

A study of the mineral parageneses leads to the following genetic conclusions. The metasomatic zones of alunitic quartzite, argillite, adularized rocks, and propylites develop as a result of substitution of mineral parageneses of internal zones for the parageneses of external zones. The opalization is superimposed on metasomatites formed previously. Halloysitization completes the process of mineral formation. The barite-polymetallic mineralization is not superimposed on metasomatites of the alunite-propylite series, but precedes them and is connected with them genetically.

GEOCHEMICAL CHARACTERISTICS OF METASOMATIC ROCKS AND MINERALS

In the present paper we will discuss some of the geochemical features of the Began deposit that shed light on the mechanism and physicochemical conditions of its development. The distribution of iron in metasomatic rocks has been investigated to gather this information. Zhukov [9, 10] has shown by theoretic modeling of metasomatism and a study of the

TABLE 3. Contents of Accessory Elements in Alunitic Ores of the Began Deposit, g/ton

Element	Began area			Dedovsk area			Mean for deposit	Mean in acid effusive rocks [4]
	I	II	III	I	II	III		
Lithium	<0,5	<0,5	<0,5	<0,5	<0,5	<0,5	<0,5	40
Rubidium	<10	<10	<10	<10	<10	<10	<10	200
Cesium	<5	<5	<5	<5	<5	<5	<5	5
Copper	32	33	120	43	32	35	41	20
Silver	2,3	4,1	3,4	1,0	1,0	1,2	2,5	0,05
Gold	<0,04	<0,04	0,05	0,04	0,07	0,05	0,04	0,0045
Beryllium	1,5	<1	<1	—	—	—	1	5,5
Strontium	80	330	370	330	372	508	304	300
Barium	6050	4600	3600	2060	980	1070	3570	830
Zinc	81,5	97	940	100	36	88	125	60
Cadmium	<5	<5	—	<5	<5	5	<5	0,5
Scandium	9,0	5,0	3,5	—	—	—	6,0	3
Mercury	0,06	0,50	1,3	—	—	—	0,49	0,08
Yttrium	<16	<16	<16	<16	<16	<16	<16	34
Boron	6	6	<6	—	—	—	6	100
Gallium	24	25	16	30	30	30	26	20
Indium	0,03	0,43	0,11	0,08	0,04	0,11	0,20	0,26
Thallium	—	—	6	2,0	0,4	14	1,9	1,5
Zirconium	155	144	119	185	200	148	162	200
Germanium	0,64	0,92	0,86	0,38	0,44	0,51	0,67	1,4
Tin	70	6	6	15	15	20	20	3
Lead	1060	1030	660	91	295	430	735	20
Vanadium	84	84	39	—	—	—	80	40
Niobium	21	18	25	49	42	35	29	20
Tantalum	0,88	0,88	1,04	2,4	1,6	1,6	1,3	3,5
Bismuth	0,45	1,05	0,20	0,25	0,26	0,44	0,60	0,01
Selenium	0,15	0,20	0,18	0,25	0,83	0,55	0,33	0,05
Rhenium	<0,05	<0,05	<0,05	—	—	—	<0,05	0,00067
Fluorine	325	455	440	400	400	400	410	800
Cobalt	<5	<5	5	<5	<5	17	5	5
Nickel	7,5	5	24	28	18	40	14	8
ΣTR	125	140	115	200	200	160	160	301

Note. (I-II) types of alunite ores (see Table 2).

natural metasomatites produced by acid lixiviation that of most rocks-forming elements, including iron, one can "identify a lixiviation region, confined to the rear parts of the column, and a deposition region, encompassing the frontal zones" [9, p. 26]. The scheme of the metasomatic process assumed by Zhukov is classical: a simultaneous growth of zones (internal zones at the expense of external zones), the motion of solutions from internal zones to external zones, etc. In the Began deposit the areas that are practically free of iron are confined to outcrops of the main fault disruptions and spread into the center of alunitic bodies from them. The iron-rich areas are in the marginal parts alunite deposits and in argillites (see Fig. 3). One can conclude that the infiltration of solutions responsible for metasomatic alteration of liparitic tuffs proceeded from the area of intersection of disjunctive structures with the day surface. From those localities the solutions migrated mainly to sideways, slightly subsiding along the path marked by the present occurrence of alunitic bodies.

In addition to the principal components, the distribution of impurity elements in alunitic quartzites is of interest. Comparison of their contents with clark levels for acid rocks (Table 3) indicates that most elements were washed out during rock alunitization. Against this background, a group of impurity elements is identified that are typical for polymetallic deposits (silver, zinc, lead, barium, copper, and mercury), which have a noticeably higher content in the Began area. The differences between the two areas in this respect indicate that heightened contents of ore elements in alunitic quartzites are evidence of the spatial connection of barite-polymetallic metallization with these rocks.

There are interesting data on detailed spatial distribution of some accessory elements in the metasomatic rocks of the Began area surrounding the barite-polymetallic ores collected by Fishkin and Chemurako [35]; these data have not been interpreted genetically. Above the upper sedimentary bed the haloes are tail-shaped, while in deep horizons they are narrow fringes around subpolymetallic veins (Fig. 5). These authors believe that in the upper alunite-barite zone, infiltrational haloes associated with infiltrational metasomatism are common. Diffuse haloes appear around the polymetallic zone [35]. The distribution of the accessory elements thus reflects the hydrodynamic regime of solutions. The rising flow of

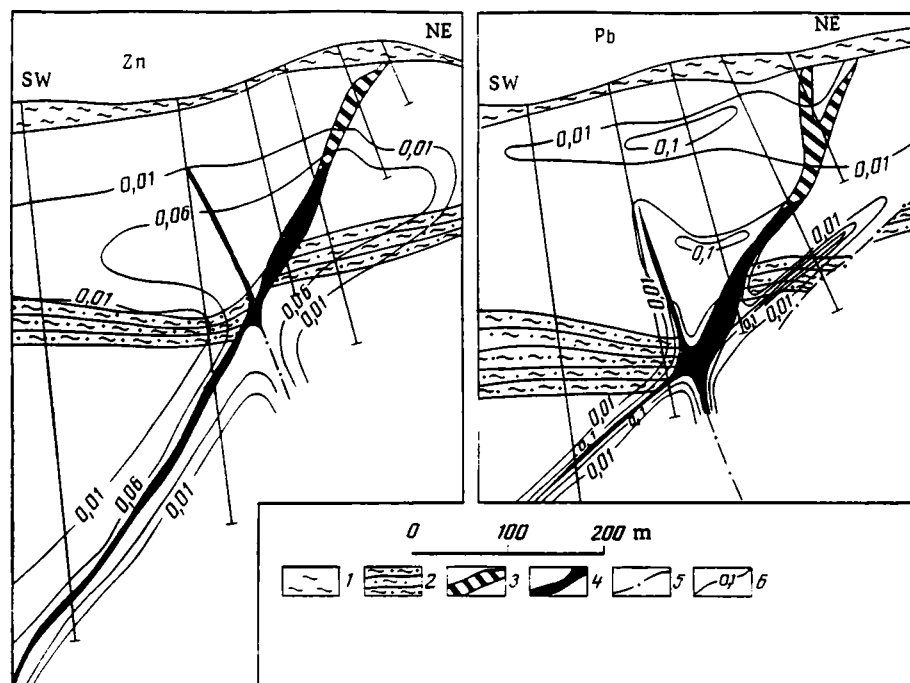


Fig. 5. Haloes of dispersed zinc and lead in the Began are [35]: (1) deluvial-alluvial sediments; (2) upper sedimentary bed amid liparitic tuffs of Dorobratov suite; (3) baritic ore zone; (4) polymetallic ore zone; (5) fissured zones; (6) isolines of element contents.

hot fluids was localized within the main fault. In deep horizons, material exchange was limited to weak diffusion transport. An infiltration of solutions away from the crack took place only in the upper horizons and was responsible for the development of large haloes (tails) disseminating accessory elements.

Potassium and sodium contents, in alunite and variations of these contents over the territory are an important characteristic of the alunite deposit. A detailed analysis of the issue has been given in [1]. The alunite of this deposit has a high potassium content; in the Dedovsk area the sodium content is somewhat higher than in the Began area, although there, too potassium is clearly predominant (in weight terms, by a factor of 10-15). Alunite of a mean composition is most common in the deposit. In some locations the potassium content is sharply reduced (by more than 20 rel. %). No regular variations of alunite content can be identified within the two areas; in particular, there is no regular depth variation of the alunite composition. Combined with the published data of experiments on the correlation between the composition of the alunite and the solution from which it was formed at various temperatures, these data confirm the predominance of potassium over sodium in the alunite-forming solution and a low temperature of alunitization, probably not higher than 100°C [1].

PRINCIPAL FEATURES OF THE GENESIS OF ALUNITE-BEARING METASOMATITES

The present theory of the genesis of the Began deposit was developed in works by Sobolev and Fishkin, Sasin, Leie, Klitchenko, Lazarenko, and other investigators [20, 23, 30, 31, 36]. Sobolev and Fishkin [31, 36] and Leie, Klitchenko, and others [23], who elaborated on their model, offered the following description of the process of formation of the alunite-bearing metasomatite rocks in the Began deposit. Hot hydrogen sulfide solutions rose from their source in the fault zones and their surrounding intact rocks. As the solutions infiltrated upward, they became oxidized with an increase in acidity and reactive capacity. The solutions reacted with surrounding rocks; as a result, unaltered liparitic tuff was replaced by corresponding metasomatic rocks, and a specific metasomatic zone evolved at each level. The reciprocal spatial positions of the altered rock facies in the section of the deposit "reflect the overall course of the evolution of the composition, properties, and conditions of post-volcanic emanations that worked as metamorphic agents along their way from the source to the day surface" [23, p. 37].

TABLE 4. Mean Volume Masses and Contents of Principal Components in Kaolinite (Dickite)- and Alunite-Quartz Rocks

Rock	Volume weight, g/cm ³	Content, %		
		kaolinite (dickite)	alunite	quartz
Kaolinite (dickite)-quartz	1,8	40	—	55
Alunite-quartz	2,2	—	35	60

For evaluating the alternative theories of the genesis of the Began alunite deposit it is necessary, first, to review at least briefly the published data on the patterns of motion of hydrothermal solutions and the development of the set of metasomatic rocks in similar geological objects.

Numerous studies of the regions of Recent postvolcanic activity [25, 34, 40-42, 45], on areas of ancient postvolcanic activity [5, 8, 33, 44], and on the dynamics of fluids and heat transfer in the development of hydrothermal deposits [26, 42, 43] suggest that a scheme of convection circulation of thermal waters is realized in areas postvolcanic hydrothermic rock alteration. Specifically, hot fluids rise in fault zones, and a zone of subhorizontal spreading usually develops in the subsurface zone on the periphery of the rising flow.

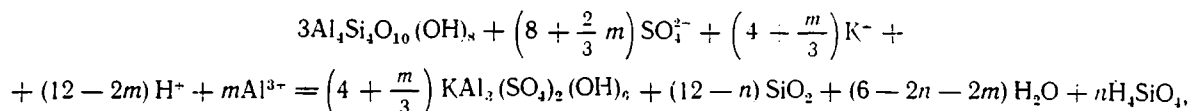
Investigators who focused on the formation mechanism of metasomatites in postvolcanic acid lixiviation [14, 24, 28, and others] found this mechanism to be consistent with the theory of metasomatic zonality [17]. Experimental studies [11, 13, 37, 46] show that when an acid solution is used to treat a magmatic rock or feldspar, a series of growing metasomatic zones is produced. Thermodynamic calculations [12, 39] confirm the possibility of simultaneous growth of metasomatic zones in secondary quartzite beds as acid solutions infiltrate through the rock. The development of typical metasomatic complexes thus is visualized as a simultaneous growth of zones under the effect of a common solution seeping through the rocks.

The formation of altered rock beds with participation of sulfur-containing solutions in postvolcanic activity areas is thus seen as resulting from the combined action to two processes: 1) convection circulation of thermal solutions and their rise to the surface through faults as a local stream, oxidation of sulfur compounds, and subsequent subhorizontal spreading; and 2) growth of the metasomatic column from the emergence site of sulfuric acid solutions in the direction of their infiltration.

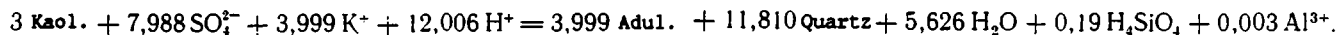
All data on the geology, mineralogy, and geochemistry of the Began alunite deposit and the published data on similar geological objects suggest the following scheme of its development. Sulfur-bearing hot fluids rose to subsurface areas (above the upper sedimentary bed) through systems of principal faults in the absence of a rising infiltration of solutions on the area. Sulfur compounds were actively oxidized near the surface, and sulfuric acid was formed. Hot fluids rising through faults in that zone then spread laterally by infiltration through liparitic tuff. The selective subsequent migration of sulfuric-acid thermal solutions was affected by the hydrogeological situation in the region — specifically, the direction of groundwater steams. The shape and orientation of alunitic deposits suggest that the predominant direction of groundwater streams in both areas was to the northeast; the "tail" of alunitized rocks points in that direction. The area where fluid-conducting faults crossed the day surface was the "core" of metasomatites in this deposit. At that location, reaction-capable sulfuric acid solutions appeared; their evolution and further spreading in the tuff bed resulted in the development of a zonal set of metasomatic rocks, consisting of propylites, adularized rocks, argillisites, and alunitic quartzites; it developed by way of an expansion of internal zones encroaching upon the external zones.

Three interconnected mineralization stages are distinguished in the development of alunite-bearing metasomatites: 1) the main stage, where a series of metasomatic rocks was formed (propylites, adularized rocks, argillisite, and alunitic quartzites); 2) a transitional zone, identified by the widespread opalization; monoquartzites were also probably formed at that time; and 3) a regressive zone, with common metahalloysitic parageneses.

The substrate of the alunitic quartzite was kaolinite (dickite)-quartz rocks. The reaction of alunite formation can be written as follows:



where m and n are molar quantities of incoming aluminum and outgoing silicon per 3 moles of decayed kaolinite in a constant volume. The values of m and n, taking into account the volumetric weight and composition of the initial and final rock (Table 4), are -0.003 and +0.19, respectively. This equation is then rewritten as follows:



Small values of m and n indicate that, generally, alunitic quartzites were formed without any significant inflow or outflow of aluminum and silicon. The alunitization process in the Began deposit took place at a low temperature, apparently below 100°C [1]. At 25°C the Gibbs potential of this reaction is -591.2 kJ/M; at 100°C the Gibbs potential is -646.9 kJ/M. The equilibrium pH, for the activity of the SO_4^{2-} ion equal to 10^{-2} , and of the other dissolved components, 10^{-3} (close to the mean values in areas of Recent alunite formation, calculated on the basis of the data of Kashkai [13]) is, at 25°C 6.35; at 100°C, pH is 5.26; the reaction, therefore, can take place even at a pH lower than that value, so that, in principle, this process could take place in the Began deposit.

Our formation mechanism of alunite-bearing metasomatites in the Began deposit thus is largely consistent with the general patterns of postvolcanic subsurface metasomatic mineral formation with participation of sulfur-containing solutions described in the literature.

* * *

The geological structure of alunite-bearing metasomatites of the Began deposit is determined by a combination of two sets of altered rocks: 1) alunitic quartzites, argillisites, adularized rocks, and propylites, forming a series of conformably occurring bodies in which alunitic quartzites in both parts of the deposit stretch and subside in the northeasterly direction from the main faults, while the other metasomatites envelop them progressively from the foot, flanks, and roof; and 2) opalized rocks and monoquartzites occurring disconformably amid metasomatites of the first set.

Three stages of mineral formation are identified. The first stage was one of simultaneous development of mineral parageneses of the internal zones at the expense of the parageneses of external zones, which gave rise to metasomatites of the first set, forming a coherent metasomatic column. During the second stage the opalization zone was formed. The third stage was one of halloysitic mineralization.

Regularities are observed in the distribution of principal and accessory elements of the alunite-bearing metasomatites. Bodies of low-iron rocks occur close to the emergence of the main faults to the day surface. Iron-rich rocks are found in the peripheral areas. The alunitic quartzites of the Began area have heightened contents of elements typical for polymetallic deposits: zinc, lead, silver, copper, and barium. Haloes of scattering of some ore elements, in the depth form narrow fringes of the barite-polymetallic zones; in subsurface horizons they appear as large tail-shaped bodies [35]. Potassium and sodium content in alunite has no regularities within each area. Amid alunitic quartzites with a consistent composition of alunite, local bodies are found with a noticeably lowering of potassium content in alunite.

The data collected and the generalizations of numerous published reports show that alunite-containing metasomatites of the Began deposit were formed by the rising of fluids along main faults. They became oxidized in subsurface environments and then spread in subhorizontal directions (mainly to the northeast); this resulted in an increase of the metasomatic column in the direction of infiltration of sulfuric acid solutions.

The theory that alunitic quartzites were formed largely by lateral infiltration of solutions rather than by their ascending flows suggests that exploration for alunitic rocks should include an analysis of the hydrogeological conditions in an area. The alunitic bodies are likely to be widespread on the side of the fluid-conducting cracks downstream from the main groundwater flow that carried sulfuric-acid thermal solutions.

The differences between subsurface metasomatites containing barite-polymetallic mineralization and similar rocks devoid of such mineralization, as determined in the Began deposit,

can be used to develop the exploration criteria in searching for this type of metallization. In particular, in the metasomatites of the Began area, dickite prevails over kaolinite, hydromica over montmorillonite, and the contents of ore elements are heightened. In the Dedovsk area, kaolinite prevails over dickite, montmorillonite is widespread along with hydromica, and the accessory element contents are much lower than in the Began area. The regular association of dickite with polymetallic mineralization is confirmed in the Transcarpathian region by the neighboring Beregov deposit, where polymetallic elements are common, while the kaolinitic mineral is mainly represented by dickite, as demonstrated by Rus'ko [29].

The existence of local areas with a lower potassium content in alunites makes it important to map such areas for detailed explorations of deposits and in mining plans, so that raw materials with chemically homogeneous alunite could be brought to the concentration mills and alumina plants.

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A NEW MIXED-LAYER PHASE IN OCEANIC IRON-MANGANESE CONCRETIONS

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UDC 552.124:551.461.6:553.324

A new mixed-layer mineral has been discovered among the Fe-Mn concretions of the Pacific Ocean, in which bouserite- and lithiophoritelike layers, commensurate in the (001) plane, alternate without order. Diffraction criteria have been deduced, which permit the identification the unordered mixed-layer in Fe-Mn oceanic concretions.

The study of the mineral composition, including the structural and crystal chemistry features, of each of the minerals in Fe-Mn concretions is an important problem, since it permits minerals to be established which are concentrators of the industrially important elements Co, Ni, Cu, and others and permits an understanding of the patterns of formation and the phase transformations of these minerals.

However, the x-ray method traditionally used for investigations of Fe-Mn concretions often does not permit a structural study to be conducted of the mineral objectives indicated or even the accomplishment of their reliable identification.

New opportunities in the crystal chemistry study of finely dispersed minerals in Fe-Mn concretions have been revealed thanks to the use of electron microdiffraction in combination with energy-dispersion analysis of individual particles [7, 8].

Our microdiffraction studies (during the analysis of x-ray data) have indicated that x-ray diffraction pictures containing intense basal reflections, with d approximately equal to 9.4-9.8, 4.65-4.9, and 2.44 Å (the 10-Å phase), may correspond to the following phases, which differ in structure.

1. Bouserite [9, 12], a layered manganese mineral (the authors of this article designate it as bouserite-I), between the Mn^{+4} octahedral layers of which are water molecules and interlayer cations (also found in octahedral coordination), compensating for the negative charge of the layers, which is created by vacant (empty) octahedra statistically distributed in these layers. After dehydration upon heating and in a vacuum, bouserite in transitional to bernebsite.

2. Bouserite-II [9], the structural model of which is distinct from that of bouserite-I in that its Mn^{+4} layers have not only singular vacancies (empty octahedra) but also chains of empty octahedra of arbitrary length, extended in accordance with the symmetry of the layers in three equivalent directions [100], [010], and [110]. Therefore, in the vacuum of the electron microscope, bouserite-II, in contrast to bouserite-I, remains a 10-Å mineral.

Institute of Ore Deposit Geology, Petrography, Mineralogy, and Geochemistry, Academy of Sciences of the USSR, Moscow. Translated from *Litologiya i Poleznye Iskopaemye*, No. 5, pp. 112-120, September-October, 1987. Original article submitted November 10, 1986.

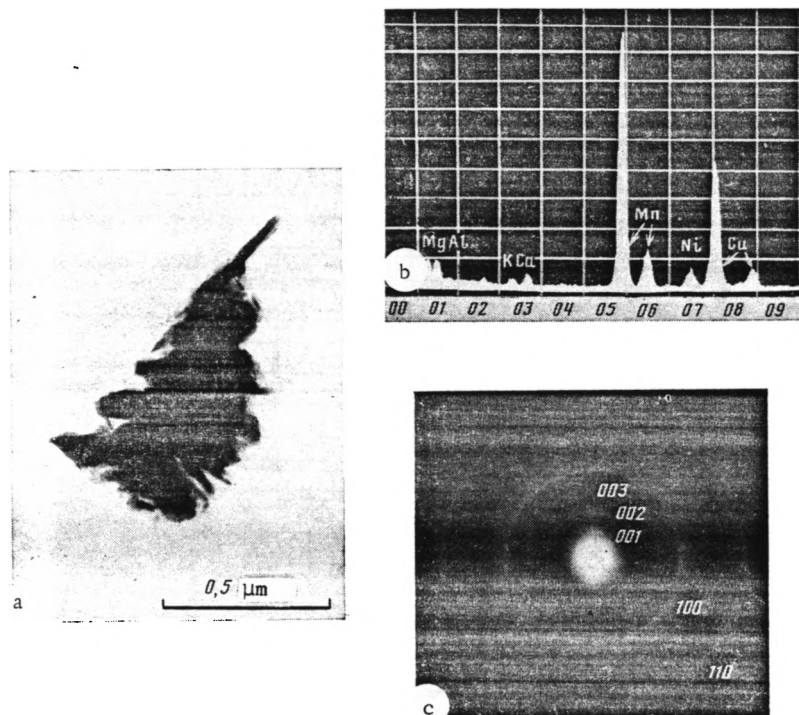


Fig. 1. Experimental data obtained for the mixed-layer phase on a JEM-100 C instrument with a Kevex-500 attachment. a) Electron-microscope picture of fine-flaky aggregates of the mixed-layer phase; b) energy-dispersion spectrum of characteristic x-ray radiation (Cu peaks from the preparation grid); c) electron-diffraction pattern (from particles with bent edges), containing $hk0$ and $00l$ reflections.

3. Asbolane [5, 6], a hybrid mineral, in whose structure alternate Mn^{+4} octahedral layers and $R(OH)_2$ layers (where $R = Ni, Co$, etc.), distinguished by the values of the basis parameters of the elementary lattices.

4. Todorokite [4, 10, 13, 14], a manganese mineral with a tunnel structure. Structurally unordered todorokites are characterized by poor x-ray diffraction pictures, similar outwardly to the diffractograms of bouserite and asbolane-bouserite.

5. Mixed-layer asbolane-bouserite [8], in whose structure asbolane- and bouseritelike (bernessitelike in vacuum) bundles alternate in disorder. In a vacuum, this phase corresponds to mixed-layer asbolane-bernessite.

The four last phases are distinctly differentiated by their microdiffraction pictures. Bouserite-I can be identified only in conjunction with the x-ray data.

Lithiophorite also belongs among the oxides of manganese, an ordered mixed-layer mineral in whose structure layers of MnO_2 and $(Al, Li)OH_2$ alternate. The repetition period of lithiophorite along the c axis is practically the same as in asbolane, except that the layers in the lithiophorite structure are commensurate in the basal plane, i.e., they have a common hexagonal elementary lattice. Compared with the above-mentioned 10-Å minerals, lithiophorite possesses a higher degree of structural ordering and is comparatively easily identified by diffraction methods.

It is natural that the minerals enumerated do not exhaust the full variety of structures possible for manganese oxides. In particular, the presence of previously unknown mixed-layer formations may be expected in oceanic Fe-Mn concretions. We discovered one such new phase in the composition of Fe-Mn concretions from the Pacific Ocean bottom at the time of the 28th voyage of the Soviet research vessel *Dmitrii Mendeleev* in 1982 [2], area station 2474 (buoy coordinates $9^{\circ}31.4'N 152^{\circ}40.3'W$). Aggregates of this phase have the form of tangled-flaky particles (Fig. 1a). The electron-diffraction patterns obtained from them (see Fig. 1c)

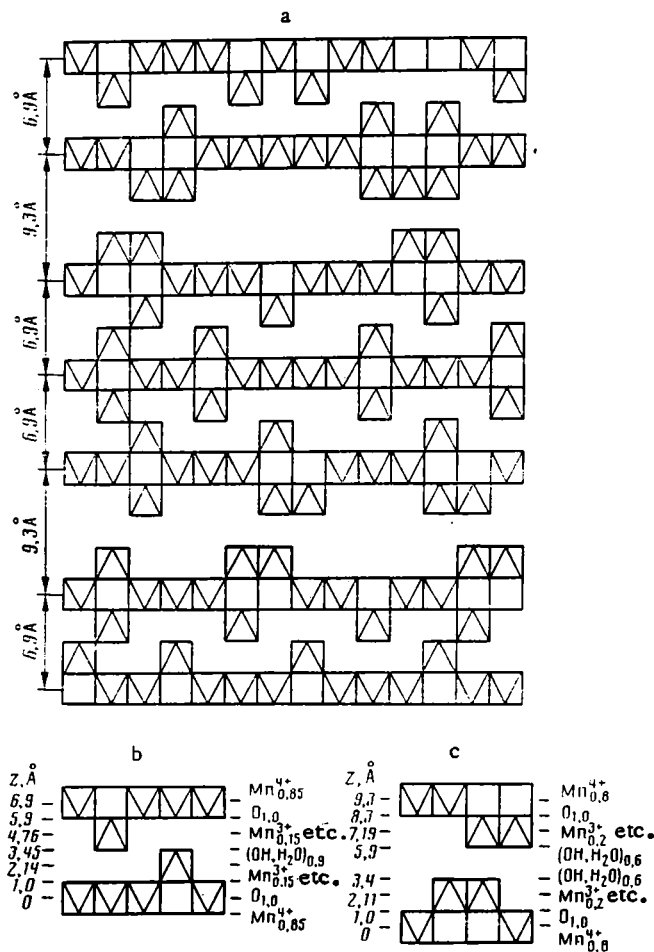


Fig. 2. Model of the Ia structure of bousserite-I-bousserite-II (a) and the structure of the corresponding components of this model (b, c).

contain basal 100 and 110 reflections, the measured interplanar distance of which correspond to the parameter of a hexagonal lattice with $a_0 = 2.84 \text{ \AA}$. In addition, three basal reflections, with d equal to 8.4-8.5, 4.60-4.67, and 3.10-3.15 $\text{\AA}$, are established on the electron diffraction patterns of all the particles. The d values for the second and third basal reflections from the center are approximately the same as the corresponding d values for the basal reflections of asbolane, since the first low-angle reflection is strongly displaced from the position of $d(001)$, equal to 9.3-9.4 $\text{\AA}$ and corresponding to asbolane, toward large angles θ . This effect leads to the appearance on the diffraction patterns of a series of basal reflections characteristic of unordered mixed-layer structures.

It must be emphasized that an analogous disposition of basal reflections has been observed on the electron-diffraction patterns of mixed-layer asbolane-bousserite [8]. In the natural state, asbolane and bousserite bundles have practically the same height; their alternation in a single structure does not disrupt the whole-number nature of the basal reflections with $d(001) = 9.4\text{-}9.8 \text{ \AA}$. However, in the vacuum of an electron microscope, the bousserite packets are compressed to $\sim 7 \text{ \AA}$, while the thickness of the asbolane constituent remains without change. This leads to an alternation in the structure of packets of differing height $\dots 7\text{-}\text{\AA}$ bousserite and $9.4\text{-}\text{\AA}$ asbolane. On the diffraction pictures, the mixed-layer nature of the mineral is revealed in the displacement of the first basal reflection toward larger angles of θ .

The principal distinction of the new phase from mixed-layer asbolane-bousserite lies in the following. Electron-diffraction patterns corresponding to the (001) plane of particles of mixed-layer asbolane-bousserite contain two nonproportional hexagonal grids of $hk0$ reflections. This confirms the presence in the structure of a mineral of the asbolane constituent,

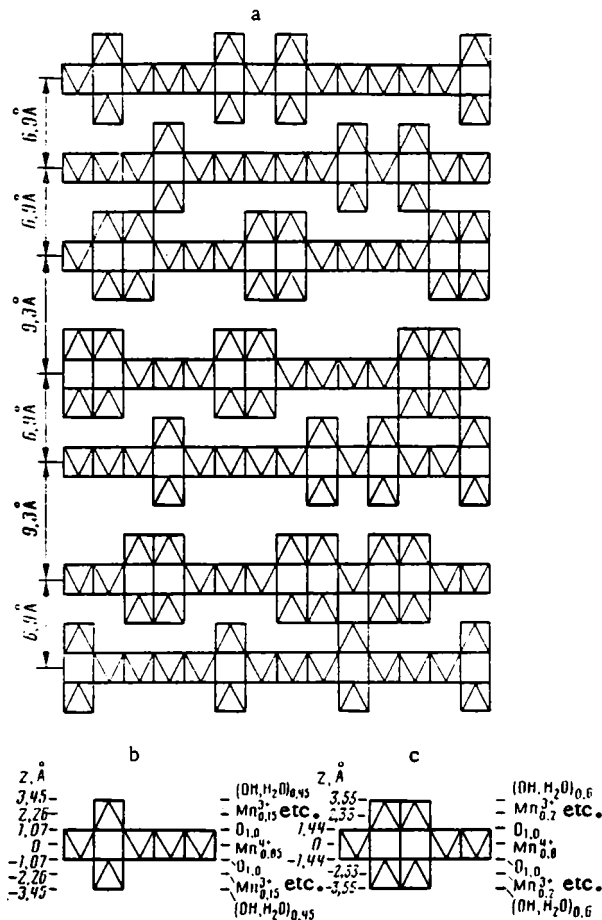


Fig. 3. Model 1b of the structure of bouserite-I-bouserite-II (a) and structure of corresponding components in this model (b, c).

formed by the joining of two types of layer, with different parameters for their elementary hexagonal lattices. As has already been noted, electron-diffraction patterns for particles of the new phase, characterizing the (001) plane, contain only one grid of $hk0$ reflections. This confirms that all the structural components may be described using a single common hexagonal lattice.

From the general crystal chemical information considered above, at least two structural models, which we shall call mixed-layer bouserite-I-bouserite-II and bouserite-I-"lithiophorite," correspond to the diffraction characteristics of the new mixed-layer phase.

By virtue of the structural similarity of bouserite-I and bouserite-II, structural transitions are possible between them, a consequence of which may be the simultaneous presence, in the same microcrystal, of interlayers (or layers) of two different types. One of these corresponds in structure to bouserite-I and the other to bouserite-II. In using the x-ray method, mixed-layer bouserite-I-bouserite-II may be characterized by the same diffraction pictures as each of the corresponding individual 10-Å minerals. However, in the vacuum of an electron microscope, the 10-Å layers of bouserite-I are transformed to 7-Å layers of bernessite, which leads to the formation of a mixed-layer structure the diffraction picture of which will contain an irrational series of basal reflections. However, in contrast to asbolane-bouserite, layers of bouserite-I and bouserite-II are characterized by the same hexagonal lattice. Therefore, the diffraction pictures of the corresponding mixed-layer phase contain one grid of hk reflections.

The other possible structure for the mixed-layer mineral being studied can be described by a model in which the layers of bouserite-I alternate in disorder with "lithiophorite" bundles, i.e., packets formed from pairs of the layers $\text{Mn}_2^{4+}\text{XO}_2$ and $\text{R}(\text{OH})_2$ (where R is Mg, Al, Mn^{4+} , Ni). These layers have a common periodicity in the basal plane by which they are

TABLE 1. Interplanar Distances d and Intensities I of Basal Reflections on Diffraction Curves Calculated for the Bouserite-I-Bouserite-II Mixed-Layer Structure (see Fig. 2, model 1a)

$W_A:W_B$							
0.2:0.8		0.3:0.7		0.4:0.6		0.5:0.5	
d	I	d	I	d	I	d	I
8.96	100	8.70	100	8.45	100	8.25	100
4.64	14	4.64	12	4.63	10	4.63	8
3.14	24	3.17	25	3.20	27	3.22	29

Note. In this and the subsequent tables, the subscript A refers to 9.3-Å layers and the subscript B to 6.9-Å layers.

distinguished from layers making up the asbolane component in mixed-layer asbolane-bouserite. The mixed-layer bouserite-I-"lithiophorite" structure in vacuum must also be characterized by a single net of hk reflections and by an irrational series of basal reflections, which appears due to interlayering of the 7- and 9.4-Å bundles in the particles.

It is evident that a geometric analysis of the electron-diffraction pattern is insufficient to draw any conclusion as to one or the other structural model. In order to solve this problem, a comparison was made of the experimental values of intensities and interplanar distances for the basal reflections with the corresponding values calculated for each of the models considered above, in accordance with the method of V. A. Drits and B. A. Sakharov [1]. Results of these calculations are presented below. Unfortunately, an exact chemical analysis of the new mineral was not successful and was limited by the qualitative data of a local x-ray microanalysis, carried out using a Kevex-5100 energy-dispersion attachment. It was established that manganese is the basic element in aggregates of the particles, as might be expected, in addition to which Mg, Al, Ni, K, and Ca were found in significantly smaller but comparable amounts (see Fig. 1b).

Analysis of Diffraction Pictures Calculated for the Mixed-Layer Structure Bouserite-I-Bouserite-II. In Figs. 2 and 3, two possible variants are presented for the structure of bouserite-I-bouserite-II. In one of them (model 1a), interlayers corresponding to bouserite-I (bernessite in vacuum) and bouserite-II alternate without order (see Fig. 2). In this model, individual layers of $(Mn_{1-x}^{+4}V_x)O_2$ (where V corresponds to the vacant octahedra) may be asymmetrically surrounded by interlayer cations (relative to the upper and lower surfaces of the layer). In Fig. 2b and c, the structure of individual components is also indicated, which are interlayered without order in the given model. In the other structure, presented in Fig. 3, the unordered alternation of bouserite-I and bouserite-II is possible (model 1b). In this case, a symmetric distribution, relative to the upper and lower surfaces of each layer, is proposed for the interlayer cations (see Fig. 3a). The structure of the corresponding components of this model are shown in Fig. 3b and c. Compression of the interlayers in a vacuum has been proposed only for layer pairs of bouserite-I. The calculation was done based on the hypothesis that the layers (or interlayers) alternate in complete disorder, and their concentrations vary from 0.7:0.3 to 0.3:0.7, with an interval of 0.1. The atomic amplitudes for the case of scattering by nearby electrons were borrowed from the work of Hirsch, Hovey, Nicholson et al. [11]. Due to the known indeterminacy of the chemical composition for the phase under study, the composition and the z coordinates of atoms in the bernessite layers were taken to be the same as in bernessite [3], and the number of vacancies in the fundamental layers in the bouserite-I composition varied with corresponding changes in the number of cations and anions in the interlayers.

In selecting the heights (thicknesses) of the alternating components, the authors were guided by the following information. In studying mixed-layer asbolane-bouserite, it was established that the position of the second basal reflection hardly depended at all on the ratio of bernessite and asbolane bundles.

In the series of electron diffraction patterns analyzed, the position of the second basal reflection with $d = 4.65$ Å did not change for the different particles. This permitted the conclusion that the height of the proposed bouserite-II layers was equal to 9.30 Å. The height of the bernessite layers (in the natural state, this is bouserite-I) was determined based on the coincidence with experimental data in the positions of the first and third reflec-

TABLE 2. Interplanar Distances d and Intensities I of Basal Reflections on Diffraction Curves Calculated for the Bouserite-I-Bouserite-II Mixed-Layer Structure (see Fig. 3, model 1b)

$W_A:W_B$							
0,2:0,8		0,3:0,7		0,4:0,6		0,5:0,5	
d	I	d	I	d	I	d	I
8,96	100	8,73	100	8,75	100	8,25	100
4,64	7	4,64	6	4,63	6	4,63	7
3,14	5	3,17	7	3,20	8	3,22	10

tions on the calculated diffraction curves. It turned out that the best correspondence between comparable interplanar distances is reached at a height of bernessite layers equal to 6.90-6.85 Å. In Tables 1 and 2 are the selection data characterizing the intensities and interplanar distances of the basal reflections calculated for unordered mixed-layer structures of bouserite-I-bouserite-II differing from one another by the content of alternating layers and the composition of the bouserite-II layers. This composition, as has already been mentioned, varied within the limits permissible from a crystal chemistry point of view. As must be expected, by increasing the concentration of 7-Å layers, a disruption occurs in the whole-number nature of the basal reflections, due to the displacement of the first of these toward larger angles θ .

If the d values measured for the observed basal reflections (Table 3) are compared with those determined on the basis of calculated diffraction curves, it may be concluded that a satisfactory correspondence is reached between them at a ratio of 6.9- and 9.3-Å components, measured within rather narrow limits, from 0.35:0.65 to 0.45:0.55. An estimate of the reflection intensities was made on the basis of the hypothesis that $I_r = F_r^2$ (F_r^2 is the square of the structure factor). A characteristic feature of all the diffraction curves calculated for models 1a and 1b with the given ratio of different types of layer and different composition for the bouserite-II layers is that distribution of basal-reflection intensities at which the first of them is three to eight times stronger than the second. This feature of intensity distribution may be considered to be the diffraction criterion for recognizing mixed-layer bouserite-I-bouserite-II phases.

Analysis of Diffraction Pictures Calculated from the Mixed Layer Bouserite-I-"Lithiophorite" Structure. The conditions for calculating the diffraction pictures are the same as those in the case considered above. The heights (thicknesses) of the alternating components were taken equal to 6.9 and 9.3 Å (Fig. 4b and c), respectively, for the bernessite and lithiophorite bundles. The calculation was done for different compositions and structures of the "lithiophorite" component: it has been proposed that brucite layers, just as in asbolane, may have a defect (island) structure. From the chemical analysis data, it follows that Mg, Al, Ni, and possibly Mn^{+4} enter into the cation group for these layers. In the calculations, the degree of defects in brucite layers was calculated with subsequent reduction in the number of anions and cations entering the elementary lattice, compared with the composition of two-dimensionally continuous Mn layers. In Table 4, values are presented for intensities and interplanar distances of reflections evaluated from the diffraction curves, which were calculated for the mixed-layer bouserite-I-"lithiophorite" structure at different contents of the 6.9- and 9.3-Å components and different degrees of defects in the brucite layers. From data presented in Table 4, it is apparent that for the regions of interest to us in concentrations of alternating 6.9- and 9.3-Å components, the intensity of the second basal reflection is two to three times stronger than the first, for a relatively high degree of perfection in brucite layers. For a defect degree equal to 0.5 (i.e., 0.5 cations...Mg, Al, Ni... entering the elementary lattice), the intensity values for the first and second basal reflections for two comparable structures become commensurate. In Table 3, experimental I and d values are presented for basal reflections which were recorded for many particles of the mixed-layer phase studied (see Fig. 1a-c). Their comparison with calculated values unambiguously confirms that the structure of the mixed-layer phase being analyzed corresponds to the model presented in Fig. 4a. Different ratios between the intensities of the first and second basal reflections, which are recorded on electron diffraction patterns of different particles, are apparently associated with variations in the degree of defects in the brucite layers. This hypothesis agrees well with the calculated data. From the

TABLE 3. Interplanar Distances d and Intensities I of Basal Reflections, Determined on the Basis of Electron Diffraction Patterns from Flakes of Mixed-layer Bouserite-I-"Defect Lithiophorite"

Particle 1		Particle 2		Particle 3		Particle 4	
d	I	d	I	d	I	d	I
8,55	100	8,50	100	8,47	95	8,4	90
4,65	90	4,60	70	4,60	100	4,55	100
3,20	10	3,20	10	3,20	10	3,20	10

TABLE 4. Interplanar Distances d and Intensities I of Basal Reflections on Electron-Diffraction Patterns Calculated for Mixed-Layer Bouserite-I-"Defect Lithiophorite" Structures

Composition of the hydroxide layer	$W_A:W_B$							
	0,2:0,8		0,3:0,7		0,4:0,6		0,5:0,5	
	d	I	d	I	d	I	d	I
(Al, Mg, Ni) _{0,3} (OH) _{1,4}	8,98	100	8,75	100	8,49	100	8,25	100
	4,65	85	4,67	80	4,68	67	4,69	54
	3,14	12	3,17	15	3,21	18	3,22	20
(Mg, Al, Ni) _{0,5} (OH) _{1,4}	8,96	70	8,73	80	8,45	100	8,23	100
	4,65	100	4,67	100	4,69	100	4,69	85
	3,13	8	3,17	12	3,21	18	3,24	16
(Al, Mg, Ni) _{0,75} (OH) _{1,3}	8,92	25	8,68	30	8,36	44	8,20	60
	4,65	100	4,67	100	4,69	100	4,69	100
	3,13	1	3,18	5	3,23	8	3,24	10
(Al, Mg, Ni)(OH) ₂	8,84	12	8,61	18	8,27	30	8,14	42
	4,65	100	4,68	100	4,70	100	4,70	100
	3,13	4	3,18	6	3,22	9	3,24	12

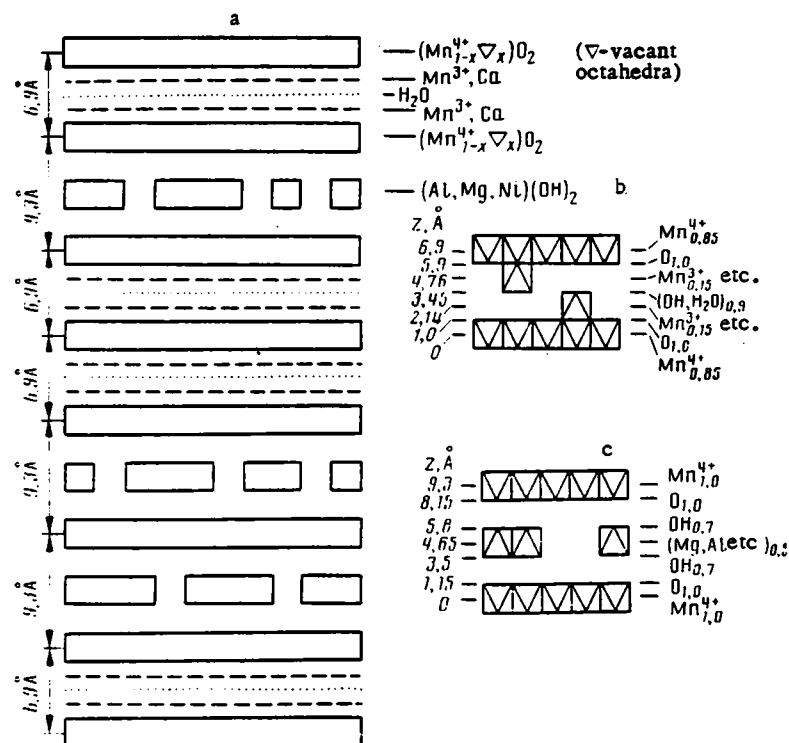


Fig. 4. Model of mixed-layer bouserite-I-'defect lithiophorite' structure (a) and structure of corresponding components for this model (b, c).

crystal chemistry point of view, the existence of mixed-layer phases of the type considered is entirely justified. It is possible that they arise as a result of the solid-phase transformation of bousierite-I, a portion of whose interlayers is transformed into brucitelike layers. They turn out to be commensurate in the basal planes of the layers, but their coincident existence in a single crystal, with the island structure of brucite layers, leads to mutual lateral adjustment, with the formation of a common two-dimensional periodicity.

Several problems arise regarding the authors' naming of the new mixed-layer phase studied. The use for one of the components of the name "lithiophorite" has no basis in strict crystal chemistry. Justification for its use may be found in the fact that this name designates a mineral known in nature in whose structure alternate layers of MnO_2 and $\text{R}(\text{OH})_2$ which are commensurate in the basal plane. The absence of lithium in the hydroxide layers is not a drawback, since althit lithiophorites are encountered. However, not only Al, but Mg, Ni, and possibly Mn^{4+} as well, enter into the cation composition of the $\text{R}(\text{OH})_2$ layers. Layers of Mg-Al composition make up the basis of hydrotalcite-manasseites, but materials have still not been described in the literature which are analogous in structural and diffraction characteristics to lithiophorite in which Mn layers alternate with Al, Mg, and Ni hydroxide octahedral layers. It is possible that they exist in nature. Evidence for this lies in some of the diffraction data obtained which may be interpreted to be the result of the epitaxial growth of asbolane and "lithiophoritelike" phases. However, monomineralic segregations of the phase being considered have not been found. Under these conditions, the authors thought it expedient to name the phase studied mixed-layer bousierite-"defect lithiophorites." The work "defect" emphasizes the island structure of the $\text{R}(\text{OH})_2$ layers, and the quotation marks draw attention to the arbitrariness noted above in the use of the name "lithiophorite,"

On the basis of the studies conducted, it is possible to formulate diffraction criteria with whose guidance it is not difficult to identify three different unordered mixed-layer minerals whose electron diffraction patterns are characterized by basal reflections in practically the same position. Mixed-layer bousierite-asbolane is distinguished from the other two by the presence of two nonproportional hexagonal grids of hk reflections on electron diffraction patterns. The mixed-layer structures of bousierite-I-bousierite-II and bousierite-I-"defect lithiophorite" are sharply distinguished from one another on electron diffraction patterns by the distribution of the basal-reflection intensities I_i . If the subscript i represents the sequential number of reflections from the center of the pattern, then for mixed-layer bousierite-I-bousierite-II, the condition $I_1 \ll I_2 \gg I_3$ must be maintained, and for bousierite-I-"defect lithiophorite" the condition $I_2 \approx I_1 \gg I_3$.

* * *

A new mixed-layer formation named bousierite-I-"defect lithiophorite" has been established in iron-manganese concretions from the Pacific Ocean bottom. Its structure consists of unordered, alternating bousieritelike layers and lithiophoritelike bundles formed of pairs of $\text{Mn}^{4+}_2\text{O}_2$ and $\text{R}(\text{OH})_2$ layers (where R = Al, Mg, Ni), the alternating layers being commensurate in the (001) plane; the $\text{R}(\text{OH})_2$ layers are of an island structure.

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GEOHERMAL INVESTIGATIONS IN THE OCEANS IN CONNECTION
WITH STUDIES ON GAS HYDRATE CONTENT

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UDC 550.836:553.981.6:551.461.6

Properties of the thermal field of submarine gas hydrate deposits are examined. An analysis of geothermal data from the Arctic Ocean is presented which shows errors in calculations relating to natural and technological heat instability. The need for geothermal investigations in research on the gas hydrate content of the ocean basins is demonstrated.

One of the important results of oceanographic research in recent years has been the discovery of the gas hydrate content of the ocean basins. Drill cores with hydrates have been recovered from holes on the continental slopes and rises of the Pacific and Atlantic oceans. Geochemical and geophysical (seismic) indicators of gas hydrate content have been found along these topographic areas in other oceans. They have been proposed on the basis of drill logs on the Arctic shelf. The occurrence of gas hydrates near the base of mud volcanoes has been demonstrated [3].

It has become apparent that gas hydrate formation is a factor in oceanic lithogenesis, much like cryolithogenesis on the continents [2]. Hydrates of gas may form monomineralic rock, which establishes the upper limit of gas hydrate saturation; they may be one of the main rock-forming minerals filling pore spaces and cementing friable clastic materials; or they may be accessory minerals with a minimal amount of gas hydrate saturation (usually under conditions of an insufficiency of gas).

The purpose of this article is to describe and demonstrate the need for geothermal studies in the investigation of gas hydrate content of the ocean floors.

Gas hydrates are solid compounds which are stable at the relatively low temperatures and high pressures (expansibilities) of gas hydrate formation (Fig. 1). Thermobaric conditions that favor the formation of gas hydrates exist almost everywhere other than the shelf beneath polar regions. If the question arises as to the depth of the zones in which hydrates may occur in the section, then the graph shows an actual thermogram of T_h and PT equilibrium diagram for hydrates (assuming P corresponds to the hydrostatic pressure at a water density of 1 g/cm^3) and the points of intersection form the boundaries of the zones in question. Of course, the accuracy of prediction depends on the reliability of the geothermal information. A solution of the inverse problem (estimation of the heat flow from data on the position of the base of gas-hydrate-bearing zones) has been presented by Yamano and others

Sevmorgeologiya Polar Geophysical Observatory, Leningrad. Translated from *Litologiya i Poleznye Iskopaemye*, No. 5, pp. 121-125, September-October, 1987. Original article submitted October 30, 1986.

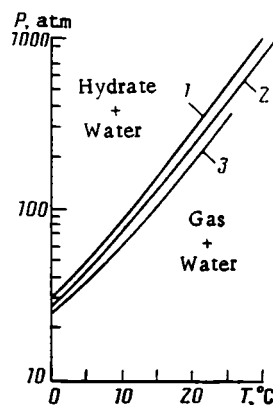


Fig. 1. Stability conditions for hydrates in the system $\text{CH}_4 + 3.5\% \text{ NaCl}$ in water (1), $\text{CH}_4 + \text{fresh water}$ (2), and $\text{CH}_4 + 7\% \text{ CO}_2 + \text{fresh water}$ (3) [8].

[8]; the base of the zone is a seismic reflection horizon that resembles the ocean floor, a "bottom simulating reflector" or BSR.* If the temperature at the seafloor is known and the temperature of the BSR is determined from the PT diagram of the hydrate, then the geothermal gradient can be calculated. Furthermore, density of the sediments can be derived from statistical relationships of seismic velocity, and heat conductance from the density. In this manner the data needed for calculation of the heat flow are obtained. The authors estimate that the maximum error of the proposed method is 25% of the absolute value, and believe that for regional studies it gives more reliable results than by single sounding measurements.†

Both of these problems, determination of the boundaries of the thermobaric zones of hydrate stability and estimation of deep heat flow at the base of this zone, could be resolved rather easily if there were not an inherent instability in the geothermal field of gas-hydrate-bearing deposits. This is similar to the instability of the frozen zone, which on the Arctic shelf and in a number of continental regions does not reflect the modern heat exchange on the sea floor or surface of the Earth, but is a relict of conditions that prevailed at least several thousand years ago. The difference is that the stability of hydrates is determined by the persistence of not only the temperature but also the pressure (and that means sea level fluctuations). In thermophysical sense, the analogy between frozen and gas-hydrate-saturated rocks is appropriate: the heat of the phase transition of gas and water in hydrate for natural hydrocarbon gases, in the temperature range $0-20^\circ\text{C}$, is $0.5-0.6 \text{ kJ per gram of water}$, which is somewhat greater than the heat of melting of ice at 0°C (0.335 kJ). Thus, gas-hydrate-bearing deposits differ from frozen, when other conditions are equal by a greater heat lag.

A characteristic feature of gas hydrates in geological environments is that they are almost always unstable, even if the temperature and sea level do not change: the formation and dissociation of hydrates are controlled by the expansibility of the gas hydrate generated. If the expansibility of the gas increases (for example if gas is generated in situ from organic matter or rises up from the depths), then hydrates are formed; if gas is leaving the system and its expansibility is thus decreased, then hydrates in the system will begin to dissociate.

The rate of these processes naturally depends on the rate of introduction and diffusion of the gas. It is difficult to conceive of a situation in which introduction and diffusion of gas in bottom sediments containing hydrates are equal. Therefore the presence of hy-

*The main reason for using the hydrate-determined BSR is the proximity of the PT characteristics of this horizon to the equilibrium curve $\text{gas} + \text{water} = \text{hydrate}$. It should be noted that the connection between the BSR and the base of the hydrate-saturated beds remains hypothetical; cases are known in which the BSR was not found in areas where drill holes revealed hydrates.

†The method described neglects the effect of hydrate saturation on seismic velocity and heat conductance of the sediments [7].

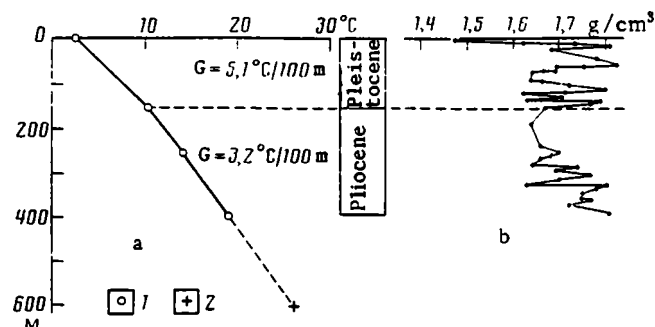


Fig. 2. Geothermal gradient (a) and sediment density (b) according to measurement in DSDP hole 533 [6]. 1) Measured temperature; 2) temperature extrapolated to the depth of the BSR.

TABLE 1

$A_{\xi}, ^{\circ}\text{C}$	$A_0, ^{\circ}\text{C}$	$\xi, \text{ m at K, m}^2/\text{sec}$		
		$1 \cdot 10^{-5}$	$1 \cdot 10^{-6}$	$1 \cdot 10^{-7}$
0.005	0.5	33	10	3.3
	0.05	16	5	1.6
0.001	0.5	44	14	4.5
	0.05	28	9	2.8

drates in submarine deposits should, as a rule, be associated with instability of the temperature field. Since hydrate formation is accompanied by the generation of heat and dissociation by the absorption of heat, positive geothermal anomalies should occur with hydrate formation and negative anomalies with its dissociation. Cases are evidently possible in which hydrates are dissociating at the base of the hydratebearing deposits while they are forming at the top, and vice versa. Hydrate formation is probably responsible for the variation in geothermal gradient in a deep oceanic drill hole (Fig. 2) in which heat is released in the upper part [6]. Drill core from this hole reveals the presence of hydrates. The boundary of geothermal effects of dissociation of hydrates in the upper part of the section, i.e., at relatively shallow depths, may be the negative heat flow in the layer overlying the hydrates.

The considerations presented above can obviously serve as a basis for the use of geothermal observations for the discovery of hydrate accumulations and an explanation of the course of hydrate forming processes. A more thorough basis for this method requires additional study, especially the mathematical modelling of heat and mass transfer during gas hydrate formation at depth; laboratory determination of the heat constant of hydrate-bearing deposits and other physicochemical parameters that would make calculations based on the mathematical models possible; and natural geothermal and other observations on standard objectives, known gas hydrate shows. At the same time, as "gas hydrate correction" should be taken into consideration in determining deep heat flow.

In addition to this, our experience shows that the application of geothermal research to the study of gas hydrate content of the seas needs improvement in the methods of observation. This is particularly true for probing methods, which provide the basis for practically all of the geothermal data from the oceans. We have analyzed the available geothermal data from the Arctic Ocean in order to determine the position of the boundary of the zone of stability of hydrates. In the process we first established that some of the measurements were made within sediments at depths considerably less than the depth (assuming accuracy of the measurement) of penetration of periodic temperature fluctuations of the bottom waters. This applies particularly to the shelf; according to hydrologic data, the annual amplitude of bottom temperature fluctuation on the Arctic shelf frequently reaches several tenths of a degree, and in individual areas, as much as several degrees. Simple calculation according to the formula, based on Fourier's first law,

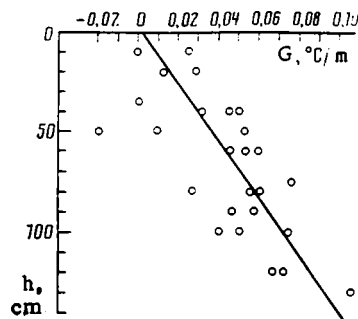


Fig. 3. Relationship of measured temperature gradient G to depth of the lower sensing unit of a probe in an area on the upper part of the continental slope of the East Siberian Sea.

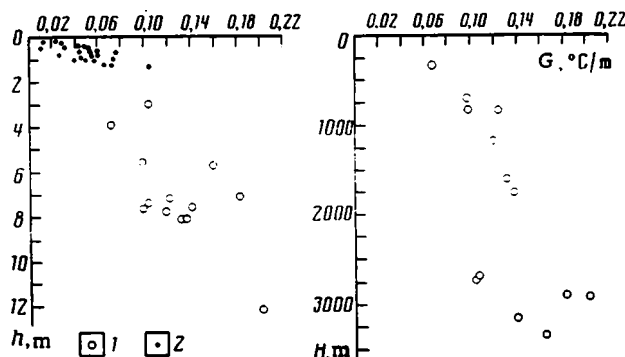


Fig. 4. Relationship of measured temperature gradient G to depth unit h and ocean depth H : 1 — northern section of the Norway-Greenland basin; 2 — upper section of the continental slope of the East Siberian Sea.

$$\xi = \sqrt{\frac{KT}{\pi}} \ln \frac{A_0}{A_\xi}, \quad (1)$$

where ξ is depth of penetration of temperature fluctuation with amplitude at the surface A_0 , period T , equal to $1/2$ year, and amplitude A_ξ , equal to the assumed accuracy of measurement (at depth ξ); K , the coefficient of temperature conductivity, indicates that under real conditions ξ is not less than 1 m (Table 1). Therefore measurements in an area of the East Siberian Sea [1], carried out in bottom sediments to a depth of 1 m, do not characterize deep heat flow. This concerns measurements in the Barents Sea along a profile from Franz-Joseph Land to the Rybachii Peninsula [4], as a result of which both negative heat flow values and magnitudes of more than 15 ETP were obtained.

The introduction of errors due to periodic fluctuations in the temperature of bottom waters can be avoided by increasing the depth of thermal probing and division of the area into districts based on hydrologic studies.

In an attempt to use geothermal data from the Arctic Ocean, the authors encountered errors in the measurements, which are mainly technological. For example, in a study of a small area on the upper part of the continental slope in the East Siberian Sea [1], the bottom temperature and coefficient of heat conductivity of deposits at essentially the same depths below sea level show that the geothermal gradient varied within a wide range: from 0.02 to 0.077°C/m. A search for the cause of this variability led to the conclusion that it was of a technological nature: the temperature gradient increased systematically with an increase in the depth of the measurements (Fig. 3); the correlation between the magnitude of the gra-

dient and the depth of the lower sensing unit proved to be statistically significant (correlation coefficient r equal to 0.65). Similar patterns appeared in an analysis of foreign data from the northern part of the Norway-Greenland basin [5], even though the study area, the depth of the sea, the variation in this depth, the variation in bottom temperature, and the probe depth in this area were considerably greater than in the East Siberian Sea. Here as well an increase in temperature gradient is found with an increase in depth of penetration of the probe (Fig. 4); for 13 readings, $r = 0.66$. At the same time, the temperature gradient also proved to correlate with depth below sea level ($r = 0.7$). The precise reason for these observed aberrant trends is not clear, but it seems likely that they are associated with an insufficiently small drift of the measuring device (along with insufficient time of observation of the probe in the environment being measured).

* * *

Geothermal studies are a necessary link in the study of gas hydrate content of the ocean basins. Heat that is inherent in gas hydrate deposits serves as a basis for the use of geothermal methods for discovery of accumulations of gas hydrates and for revealing the trend of processes in gas-hydrate-bearing rocks. Application of these methods should draw upon mathematical models, laboratory experiments, and directed field observations on standard objectives. Moreover, methods of marine geothermal measurements need improvement: errors associated with natural and technological thermal instability should be eliminated.

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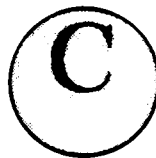
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